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1 AUTHOR:

Richard Stephen Berry
University of Chicago

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Ultraviolet Spectrum of Dibenzene Chromium Vapor*†

R. Stephen Berry

Sterling Chemical Laboratory, Yale University, New Haven, Connecticut

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The ultraviolet spectrum of dibenzene chromium vapor has been observed under medium resolution conditions. At least three separate band systems are found, at least two of which display progressions of the totally symmetric vibration frequencies. Possible assignments are considered and compared with alternative level structures. It is concluded that the $3de_{2u}$ level probably lies below the metal a_{1g} orbital, and that term splitting may play a considerable role in determining the order of the excited states.

INTRODUCTION

THE absorption spectrum of dibenzene chromium vapor has been investigated in the region 2100–6000 Å. This study was undertaken because of recent interest in the electronic energy levels and structure of dibenzene chromium[1-6] and more specifically, because the reported ultraviolet absorption spectrum of dibenzene chromium itself in cyclohexane[5] shows none of the banded character found in the spectra of a number of other chromium-arene molecules.[7,8] Proposed level schemes for these molecules imply that all their spectra should display several reasonably strong band systems in the visible and near-uv region. Only dibenzene chromium itself failed to show such a spectrum; the absorption spectrum reported by Feltham[5] showed a very broad peak having a maximum at about 3200 Å and a shoulder in the 4000 Å region, and a second, much weaker maximum at about 6500 Å. Other spectra of solutions and crystals of compounds of this kind characteristically show several absorption bands: six for the one Cr(0) compound reported, and seven for the Cr(I) systems.[7,8] The vapor spectrum of dibenzene chromium was examined in hopes that it would display more structure than the solution spectrum, enough perhaps to display separate electronic transitions.

EXPERIMENTAL

The sample of dibenzene chromium was supplied by Dr. R. L. Pruett of the Union Carbide Chemicals Company. The material was transferred into the sample cell in an atmosphere of nitrogen; the cell was evacuated to remove volatile contaminants; argon was ad-

mitted to give a pressure of approximately 30 cm Hg at 25°C. The sample cell itself was a fused silica tube, 25 mm in diameter and about 24 in. long, with clear fused silica end windows attached with Apiezon W wax. The middle third of the tube was wrapped with asbestos, wound with Nichrome heating wire and wrapped with a second layer of asbestos. A copper-constantan thermocouple measured the temperature of the tube.

Solution spectra and preliminary gas-phase spectra were taken on a Cary model 11 spectrometer. The final gas-phase investigation was carried out with a Bausch & Lomb medium-quartz spectrograph. A variety of photographic plates were used to investigate various regions of the spectrum: Eastman 103–0 plates for general use, Ilford Q–3 and HPS for the far ultraviolet, and Ilford HPS and R–50 plates for the visible region. The light source for the photographic work was a fused-silica capillary flash lamp, through which approximately 90 joules were discharged in about 30 μsec.

The first spectra showed the presence of a small amount of benzene; after the cell and sample had been warmed and re-evacuated, no traces of benzene would be seen in the spectrum. When the cell was reopened after a number of spectra had been taken, crystals of the sublimed dibenzene chromium were removed from the cell and dissolved in cyclohexane. The spectrum of this material was essentially indistinguishable from that reported by Feltham.[5]

The absorption spectrum of dibenzene chromium vapor is dramatically different from that of the solution. Instead of a broad, featureless single peak, the spectrum shows at least three distinct band systems, which in turn have well-defined vibrational structure. Table I lists the prominent maxima. These are rather diffuse, and permitted measurement to only about ±3 Å in the middle of the spectrum. Representative spectra are shown in Fig. 1.

The absorptions described here are classified into three systems; system I, whose strongest band lies at 3748 Å; system II, a diffuse system with a maximum near 3050, and with definite bands only at the short-wavelength end; and system III, which actually includes bands of three groups, a long progression in the 2820–2670 region with the strongest maximum at

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TABLE I. Absorption maxima of dibenzene chromium.[a]

Long wave bands $\lambda(A)$	System I	System II	System III	
4370	3907 ?	3010	(a) 2823	
4315	3833	2970±10	2800 vs	
4156	3781	2946	2781 s	
	3748 vs	(plus diffuse	2760 b	
	3711 s	absorption at	2730 ms	
	3674	longer wave-	2711	
	3640 s	lengths)	2694	
	3606		2669	
	3571			
	3533		(b) 2604	
	3480 ?		2570 s	
	3365		2552 ms	
			2465 s	
			2450 ms	
			2408 s	
			2395	
			2373	
			2343	
			2332	

[a] vs, very strong; s, strong: b, broad; ms, moderately strong.

2800, at least three more bands at about 2570, and another long, diffuse series between 2465 and 2332 A. Of these, the middle group extends into a region of silicon absorption lines of the lamp which prohibits investigation of the 2500 A region. The classification of systems was chosen to correspond to that used by Yamada et al.[7,8] in their investigation of the solution and crystal spectra of chromium arene compounds. Our photographic study did not extend to long enough wavelengths to search for the very weak band at about 6500 A reported by Feltham; we did find such a band in the solution spectrum. This band is presumably the spin-forbidden band of references 7 and 8.

The gas-phase spectrum failed to show any strong absorption in the 2100 A region. Presumably the strong $\pi\rightarrow\pi^*$ transition denoted as IV in reference 7 lies at a wavelength too short to be detected with our system; that is, it must fall beyond 2100 A.

System II has only three well-defined bands, all far from the center of the absorbtion, so one may be hesitant to try to associate the frequency differences with any of the observed vibration frequencies of dibenzene chromium.[9,10] Systems I and III, on the other hand, have very clearly defined progressions which can probably be associated with known vibrations. In both systems, the most obvious frequency is the ν_{21} totally symmetric vibration of the rings against the central chromium. This has been estimated as 280 cm^{-1}.[9] The estimate we make from systems I and III is 260–270 cm^{-1}.

System I also shows the ν_{11g} totally symmetric CH bending frequency, previously found to be 790 cm^{-1} in dibenzene chromium iodide[9,10] and estimated at about 787 cm^{-1} from the present work. One narrow band at

[9] H. P. Fritz, W. Lüttke, H. Stammreich, and R. Forneris, Ber. deut. chem. Ges. 92, 3246 (1959).
[10] R. G. Snyder, Spectrochim. Acta 15, 807 (1959).

3365 A looks similar to the bands of system I and lies 3037 cm^{-1} to the violet of the strongest band of this system. It may be associated with the ν_{2g} symmetrical CH stretching mode; the corresponding frequency in $(C_6H_6)_2CrI$ is 3095 cm^{-1}. The band at 3781 A is probably a "hot" band from the first excited vibrational state of the ν_{21} symmetrical valence mode, according to the analysis below.

The absorption at wavelengths greater than 3781 A might be due to more excited vibrations in system I. We prefer, however, to assign this as a separate electronic transition. This point is discussed further in the next section.

Differences taken from system III show not only ν_{21} but also a 911 cm^{-1} frequency which may be the ν_{1g} symmetric ring-breathing frequency of the upper state. Frequency measurements of the shorter wavelength bands attributed to this system are complicated by emission lines of the light source. Nonetheless the ν_{21} frequency seems to appear throughout the system. The band at 2823 A seems to be a hot band of this vibration.

The extended 260 cm^{-1} progressions have their strongest band near but not at the long wavelength end of the progressions. Moreover, the intensity in the bands on the red side of the most intense bands seems to be more sensitive to temperature than the intensity on the violet side. These observations indicate that the short-wavelength parts of the progressions are due to upper-state levels, and the long-wave side, to hot bands. This, in turn, indicates that in series I and III, at least, the electronic excitation produces no drastic changes in the ring-metal bonds. Since the frequency differences of the bands in these series seem to be those of totally symmetric vibrations, we believe these to be allowed transitions involving nonbonding orbitals.

DISCUSSION

In a previous note, an attempt was made to assign the spectra of several compounds of chromium and benzene.[6] The assignments were made in terms of a strong-field formalism, and were carried out for the threefold-symmetric symmetry reported for dibenzene chromium in the crystal and for the sixfold symmetry which the molecules are supposed to exhibit in fluid phases. Only the orbital levels were considered; term-splitting was not considered except as it affected the intensities of various bands. The most probable assignments, it was felt, were as follows. Referring to the bands in the notation of Yamada et al.,[7,8] and using D_{6h} symmetry for the molecule, we have

band I: $3de_{2g}(^1A_{1g})\rightarrow 4pe_{1u}'(^1B_{1u}, {}^1B_{2u}, {}^1E_{1u})$;

band II: $3da_{1g}(^1A_{1g})\rightarrow 4pe_{1u}'(^1E_{1u})$,

$\qquad e_{1u}(^1A_{1g})\rightarrow 3de_{1g}'(^1A_{1u}, {}^1A_{2u}, {}^1E_{2u})$,

$\qquad 3de_{2g}(^1A_{1g})\rightarrow 4pa_{1u}'(^1E_{2u})$;

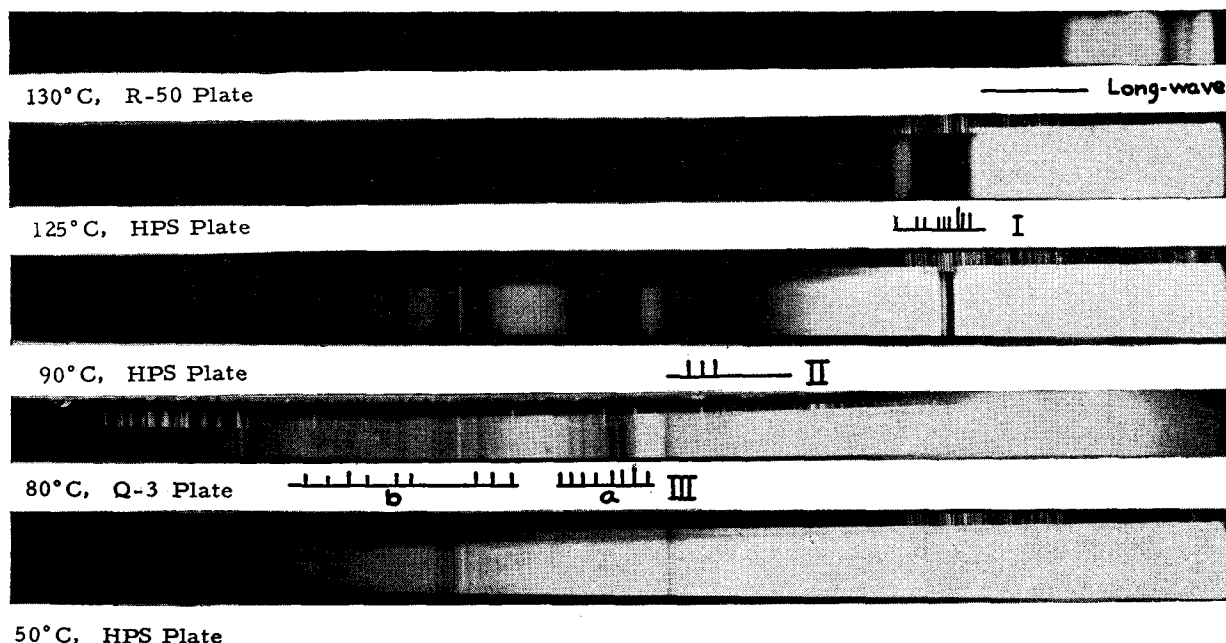band III: $3da_{1g}(^1A_{1g})\rightarrow 4pa_{1u}'(^1A_{1u})$.

FIG. 1. Representative spectra of dibenzene chromium vapor.

The transitions listed include all those below the $\pi e_u \rightarrow 3d a_{1g}'$ and $\pi \rightarrow \pi^*$ transitions, having components allowed in D_{3d} symmetry. In D_{6h} symmetry, only the $^1A_{1g} \rightarrow {}^1A_{1u}$ and $^1A_{1g} \rightarrow {}^1E_{1u}$ transitions are allowed; they are polarized parallel and perpendicular to the sixfold axis, respectively. According to this assignment, in D_{3d} symmetry, band I has a z component as well as one with x, y polarization. An alternative assignment was given, based on placement of the filled $a_{1g}(3d+4s)$ orbital above the $3de_{2g}$. This alternative, harder to reconcile with the solution spectra, better explains the observed g value of the paramagnetic $(C_6H_6)_2$ CrI molecule. The only major change in the assignments of the spectral bands is the interchange of the $e_{2g} \rightarrow e_{1u}'$ and $\pi e_{1u} \rightarrow e_{1g}'$ bands. This in turn changes the polarization expected for band I in D_{6h} symmetry. In the former assignment, the transition moment of band I is polarized parallel to the planes of the rings and band II contains both parallel and perpendicularly polarized components. In the latter assignment, band I has its moment perpendicular to the rings, and band II is due entirely to a parallel transition. Let us also consider the possibility that dibenzene chromium in solution is threefold symmetric, as it is in the crystal. Then both bands would have parallel and perpendicular components in either scheme.

If band I of the solution spectra is indeed due to the same transition as system I of the vapor spectrum of dibenzene chromium itself, and if system I appears as a distinct uv-fluorescent system when dibenzene chromium is dissolved in a rigid glass, then a measurement of the fluorescence depolarization of system I would demonstrate whether the dibenzene chromium molecule has D_{6h} or D_{3d} symmetry (in the glass, at

least), and, if its symmetry is sixfold, whether the $^1E_{1u}$ or $^1A_{1u}$ excited state lies lower.

The amount of information in the vapor spectrum of dibenzene chromium prompts us to re-examine our level scheme, and to try to correlate the observed spectrum with the binding in this and perhaps other sandwich compounds. One recent limited molecular orbital calculation, for example, suggests that the major contribution to the metal-ring bond in $(C_6H_6)_2Cr$ is the mixing of the $3de_{2g}$ orbitals of the chromium atom with the empty ring orbitals of the same symmetry.[1] The same effect has been inferred by Levy and Orgel[4] from their discussion of the energetic order of the a_{1g} and e_{2g} orbitals of ferricinium ion and dibenzene chromium iodide. This would imply that the e_{2g} orbital is strongly bonding, and that removal of an electron from this orbital would weaken the bond between rings and the chromium atom.

If the e_{2g} orbital is indeed a strongly bonding orbital, then it is difficult to reconcile the assignment of system I as an $e_{2g} \rightarrow e_{1u}'$ transition. It now seems more probable, in view of the appearance of the bands system and of the ν_{21} vibration in particular, that it arises from the $\pi e_{1u} \rightarrow 3de_{1g}'$ transition, and that the a_{1g} orbital does indeed lie above the e_{2g}. Shustovorich and Dyatkina[1] compute the a_{1g} energy slightly lower than the e_{2g}, but point out that the two levels are so close that their calculation cannot be trusted to give the exact order. Levy and Orgel,[4] on the other hand, conclude that the a_{1g} orbital must be at least 2.9 ev above the e_{2g} if the ground state of dibenzene chromium iodide is $^2A_{1g}$. Previously, the $e_{2g} \rightarrow e_{1u}'$ assignment was preferred because the alternative was essentially to say that band I was due to a charge-transfer process, which

seemed improbable according to the solution spectra. Now, the vapor spectrum shows system I to be strong, and to display all the totally symmetric vibrations except the carbon-carbon ring-breathing frequency. This fits nicely with the notions that an electron is removed from a orbital and placed in a metal orbital, and that neither of the orbitals involved contributes strongly to the ring-metal bond.

If we reassign band I to the $\pi e_{1u} \rightarrow 3de_{1g}'$ transition, then band II is quite naturally attributed to the $3de_{2g} \rightarrow 4pe_{1u}'$ on the basis of its diffuse structure. On the other hand, the center of gravity of the excited configuration of this transition should fall at higher energies than that of the $3da_{1g} \rightarrow 4pe_{1u}'$ excitation. We must therefore suppose that the term splitting within the $e_{2g}{}^3 e_{1u}'$ configuration is sufficient to push its $^1E_{1u}$ component below the state coming from the $a_{1g} \rightarrow e_{1u}'$ excitation. But this state is also a $^1E_{1u}$ state; now we are faced with satisfying the noncrossing rule. It seems, therefore, that the character of the first excited $^1E_{1u}$ state may change from being dominated by an $e^4{}_{2g}a_{1g}e_{1u}'$ configuration in a strong-field approximation to being predominantly $e_{2g}{}^3 a_{1g}{}^2 e_{1u}'$ when term-splitting and configuration mixing is included.

This change might be observable as a change in the appearance of systems II and III if the benzene rings of dibenzene chromium were replaced by rings completely substituted, say, with fluorines.

It is not possible to say at present whether system III is actually composed of one, two, or three electronic transitions. From the appearance of the band structure, it seems improbable that three transitions contribute. This argues for the regular-hexagon structure of the benzene rings, since if the symmetry were D_{3d}, we would have three and not just two low-energy allowed electronic transitions to assign. If there are two allowed transitions, then the lower-energy one, around 2800 A, is presumably the $^1A_{1g} \rightarrow {}^1E_{1u}$ transition due primarily to the $a_{1g} \rightarrow e_{1u}'$ transition and the bands at shorter wavelengths are due to the $a_{1g} \rightarrow a_{1u}'$ excitation. These transitions are polarized parallel to the ring plane and perpendicular to it, respectively, so that again, they might be distinguished experimentally.

Finally we can add one more factor which lends more support to the identification of system I as a $\pi e_u \rightarrow 3de_{1g}'$ transition, and thereby, to the placement of the metal a_{1g} orbital above the $3de_{2g}$. At high temperatures (about 120° or more) diffuse absorption sets in to the red of system I. This absorption is probably too widespread to be part of the same system, although it does overlap system I. There are two maxima on the red side of a broad, intense diffuse region, and another, somewhat stronger, on the violet side. If we identify system I as due to the $\pi e_{1u} \rightarrow 3de_{1g}'$ transition, we find that of the three terms derived from the excited configuration, the transition to one ($^1A_{1u}$) is allowed electronically, and transition to one other ($^1A_{2u}$) is electronically forbidden but becomes vibrationally allowed through the action of a low-frequency vibrational mode. Specifically, the $^1A_{2u}$ state can be reached from the first excited vibrational state of the a_{2u} asymmetrical ring-metal stretching mode, which lies 459 cm^{-1} above the ground state.[9] The alternative assignment gives three excited states of which one is again allowed, but here, neither of the other two find any low-frequency vibrations which could make them become allowed.

We summarize our results by presenting the spectral assignment which, according to this analysis seems most probable. Unobserved states are placed in brackets, and the vibrationally allowed, electronically forbidden state in braces.

System I:

$$e_{1u}(^1A_{1g}) \rightarrow 3de_{1g}'(^1A_{1u}) \{^1A_{2u}\}[^1E_{2u}];$$

system II:

$$3de_{2g}(^1A_{1g}) \rightarrow 4pe_{1u}'(^1E_{1u})[^1B_{1u}, {}^1B_{2u}];$$

system III: (long-wave bands)

$$3da_{1g}(^1A_{1g}) \rightarrow 4pe_{1u}'(^1E_{1u})$$

system III: (short-wave bands)

$$3da_{1g}(^1A_{1g}) \rightarrow 4pa_{1u}'(^1A_{1u}).$$

Further work, particularly utilizing fluorescence from a glass if this is possible, would be necessary to test this assignment.