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OXYGEN INDUCED TRIPLET STATE TRANSITIONS OF BENZENE IN CRYOGENI--ETC(U)
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⁶ OXYGEN INDUCED TRIPLET STATE TRANSITIONS OF BENZENE
IN CRYOGENIC SOLUTIONS

by

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OXYGEN INDUCED TRIPLET STATE TRANSITIONS OF BENZENE
IN CRYOGENIC SOLUTIONS*

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ABSTRACT

A new way of investigating the oxygen induced triplet state transitions of simple organic molecules is presented. The method involves dissolving the organic along with oxygen in hydrocarbon liquids such as propane, ethane, or propene. Both ${}^3B_{1u} \leftarrow {}^1A_{1g}$ and ${}^3E_{1u} \leftarrow {}^1A_{1g}$ transitions of C_6H_6 and C_6D_6 are studied in this work. These results indicate that both triplet states and their vibrational spacings are quite sensitive to the environment. The suggested dominant feature of the ${}^3B_{1u}$ state of C_6H_6 is ν_8 (916 cm^{-1}) of e_{2g} symmetry. Observed triplet state intensity enhancement is believed to be due to a non-statistical oxygen/benzene van der Waals complex formed in the low temperature liquid.

A

I. INTRODUCTION

The first triplet state absorption of benzene ($^3B_{1u} \leftarrow ^1A_{1g}$) has been observed in pure crystal^{1a,b} and O_2 perturbed systems.² The origin of the $^3B_{1u}$ state has been observed around $29,600\text{cm}^{-1}$ for both environments due to the breakdown of D_{6h} selection rules. However, the dominant series observed in the $^3B_{1u}$ state absorption are superficially different in each environment and have thus been assigned differently. In the pure crystal the dominant series is the pseudo - Jahn Teller active e_{2g} mode ν_8 (240cm^{-1}). In the O_2 perturbed gas and matrix studies the dominant series has been assigned as the totally symmetric ν_1 ($\sim 900\text{cm}^{-1}$). These apparently conflicting results and the presumed environmental sensitivity of the benzene $^3B_{1u}$ state have sparked our interest in reinvestigating such transitions in cryogenic liquids.³

The second triplet state of benzene has been identified as the orbitally degenerate $^3E_{1u}$ state and has been theoretically predicted to be located between the $^3B_{1u}$ and $^1B_{2u}$ states.⁴ Experimental observations have been made in pure and O_2 -mixed crystals; however, weak and broad features have made it impossible to analyze these data in any detail. Nonetheless, the irregular band locations of the pure and O_2 -mixed system, like those for the $^3B_{1u}$ state, make it quite clear that the Jahn Teller active $^3E_{1u}$ state is also strongly dependent on its environment. Hence, the simultaneous observation of C_6H_6 (or C_6D_6) $^3B_{1u}$ and $^3E_{1u}$ states in cryogenic liquids not only demonstrates a new reliable technique for the study of molecular triplet states but also serves as a direct comparison with other methods to elucidate environmental effects on triplet states.

In previous cryogenic liquid solution experiments³, C_6H_6 absorption spectra of the $^1B_{2u} \leftarrow ^1A_{1g}$ transition were studied in liquid N_2 , CO , CF_4 , CH_4 , C_2H_6 , C_3H_8 and NF_3 . Three conclusions from these previous experiments are important for our present work. First, the appearance of a very weak origin (0,0)

transition indicates only a slight deviation from D_{6h} symmetry due to the presence of the cryogenic liquid. Second, the dominant vibronic series involve the e_{2g} modes ν_6 (very intense), ν_8 , ν_9 , and ν_7 ; as is well known, ν_6 (C-C-C banding mode) effectively couples the ${}^1B_{2u}$ and ${}^1E_{1u}$ electronic states. Third, nonequilibrium solute aggregation occurs during low temperature deposition of cryogenic liquid solutions.^{3b} Based on these three observations, one can anticipate that for low temperature deposition, the cryogenic liquid C_3H_8 may trap the O_2/C_6H_6 complex and that, like the ${}^1B_{2u}$ state, the induced ${}^3B_{1u}$ state absorption should possess strong vibronic origins of e_{2g} symmetry (especially ν_8) with possibly a much weaker solvent or complex induced origin.

II. EXPERIMENTAL

Sample preparation and instrumental set up are described in previous reports.³ C_6H_6 (Fischer Gold label) and C_6D_6 (Merck, Sharpe and Dohme) are further purified by vacuum distillation over potassium to remove water and other oxygen containing impurities. C_3H_8 and O_2 (research purity, Matheson) are further purified by distillation through cold trapped 4A molecular sieve. The absorption cell (3.8cm pathlength) is attached to a Cryodine mechanical helium refrigerator (CT1-350). Temperature of the cell can be controlled from 12K to room temperature by a Lake Shore DTC-500SP temperature controller.

Solubility of benzene in liquid C_3H_8 at 87K is a critical factor in these experiments. It has previously been determined that C_6H_6 (C_6D_6) is soluble in C_3H_8 to about 100 ppm at 87K. At such concentrations triplet state absorptions are, of course, not observed. It is necessary to have O_2 present in the solution to enhance the triplet state transitions through the well known charge transfer mechanism. The addition of roughly 1000 ppm O_2 to the solution does not affect the solubility of benzene in liquid C_3H_8 as O_2 is miscible with C_3H_8 in this concentration range.

In the C_6H_6 (C_6D_6)/ O_2 / C_3H_8 experiments, gas phase C_6H_6 (C_6D_6) and O_2 are mixed in a 15ml manifold and then, together with C_3H_8 , are rapidly deposited into the precooled absorption cell at 70K. Absorption spectra are taken for clear solutions at 87K.

III. RESULTS

Figures 1 and 2 show the C_6H_6 spectra of $^3E_{1u} \leftarrow ^1A_{1g}$ and $^3B_{1u} \leftarrow ^1A_{1g}$ transitions, respectively. Figure 3 shows the spectrum of the C_6D_6 $^3E_{1u} \leftarrow ^1A_{1g}$ transition. The estimated ratio of C_6H_6 (C_6D_6): O_2 : C_3H_8 is 1:10:10⁴. Table I summarizes the observed frequencies. The data reported are based on many experiments whose values are averaged. For such weak features, sample to sample reproducibility and the simultaneous observation of both triplet states are important factors in the confidence level of the assignments.

In order to insure that the observed spectra are due to the O_2 induced triplet state transitions of benzene, the following experiments have been carried out. Two component experiments, at the same concentrations as the three component experiments, show that in order to observe these tabulated features, all three components must be present. Moreover, in the 2600 Å region the (very weak broad) O_2 Herzberg bands are observed but they do not coincide with the $^3E_{1u} \leftarrow ^1A_{1g}$ assigned features. In the three component system, the Herzberg bands are not observed, as the $^1B_{2u} \leftarrow ^1A_{1g}$ C_6H_6 transition overlaps them to some extent but also because the O_2 - O_2 pairs are probably more weakly bound than the C_6H_6/O_2 complex. No O_2 related features appear in the $^3B_{1u} \leftarrow ^1A_{1g}$ region.

IV. DISCUSSION

Table II gives a comparison of the ${}^3E_{1u} \leftarrow {}^1A_{1g}$ absorption features of O_2/C_6H_6 (C_6D_6)/ C_3H_8 , the pure crystal, and other O_2 -perturbed systems. Variation of band positions among these three data sets may be due to a large environmental sensitivity displayed by the Jahn Teller active ${}^1E_{1u}$ system. The origin of the ${}^3E_{1u}$ state has not been positively identified, either in this or in previous work. However, since an $E_{1u} \leftarrow A_{1g}$ transition is dipole allowed in D_{6h} symmetry and e_{2g} modes are Jahn Teller active in E_{1u} , one can surmise that the first feature is the origin and the second one is the first quantum of ν_6 (or possible ν_8).

The ${}^3B_{1u} \leftarrow {}^1A_{1g}$ transition of C_6H_6 (C_6D_6) has been studied in the O_2 -perturbed gas phase and matrix environments, and in the pure crystal. A weak origin has been observed and assigned in these systems. However, the dominant series for the O_2 -perturbed and crystal spectra have been treated in quite a different manner.

In the pure crystal system the intense absorption series involve the e_{2g} modes ν_8 , ν_6 , and ν_9 with the major feature ν_8 (CH stretching) assigned a frequency of 240cm^{-1} . Theoretical calculations confirm that the effective vibronic coupling between ${}^3B_{1u}$ and ${}^3E_{1u}$ is via the ν_8 mode and conclude that ν_8 may have its frequency depressed considerable in the presence of this strong pseudo Jahn Teller or Herzberg Teller coupling. Moreover, phosphorescence data from C_6H_6/C_6D_6 mixed crystals⁶ also indicate the dominant nature of ν_8 for the ${}^3B_{1u}$ state intensity.

For the O_2 -perturbed systems, on the other hand, the observed $\sim 900\text{cm}^{-1}$ progression built on the origin has been previously assigned to be a ν_1 (a_{1g}) series. This assignment is based solely on the idea that a 900cm^{-1} mode is close to the ground state and ${}^1B_{2u}$ state value for ν_1 . The presence of O_2 has been assumed to lower the D_{6h} symmetry of C_6H_6 (C_6D_6) to probably D_{2h} , rendering the totally symmetric origin progression allowed. However, this

scheme ignores two points: 1) it is unlikely that the ν_8 progression, even in this lowered symmetry system, would disappear; and 2) the $\sim 900\text{cm}^{-1}$ progression is highly irregular.²

From the above argument, it would seem that in the presence of O_2 , the $^3\text{B}_{1\text{u}}$ state of benzene loses its $\text{D}_{6\text{h}}$ character completely. This, however, does not appear to be the case in the cryogenic liquid O_2 -perturbed systems. First, the same $^1\text{B}_{2\text{u}} + ^1\text{A}_{1\text{g}}$ spectra are observed with or without even large amounts (10^3 ppm) of O_2 in the propane. This implies that $\text{D}_{6\text{h}}$ symmetry still holds for C_6H_6 even in the $\text{O}_2/\text{C}_6\text{H}_6$ complex. Second, neither the origin nor a $\sim 900\text{cm}^{-1}$ progression has been identified in the present study. This negative evidence calls into question the nature of the 900cm^{-1} series observed in the gas and matrix O_2 -perturbed investigations. The most probable explanation for these data is that the band at $(0,0) + 900\text{cm}^{-1}$ is ν_8 and the irregular series built on this is 8_0^n or $8_0^1 1_0^n$ as given by the elegant crystal results. In this reinterpretation, the presence of O_2 , instead of destroying the $\text{D}_{6\text{h}}$ nature of the $^3\text{B}_{1\text{u}}$ state, at most shifts the frequency of ν_8 from 1450cm^{-1} ($^1\text{B}_{2\text{u}}$) to roughly 900cm^{-1} in the $^3\text{B}_{1\text{u}}$ state. Moreover, a good deal of this frequency shift is probably attributable to the pseudo Jahn Teller or Herzberg Teller coupling between the $^3\text{B}_{1\text{u}}$ and $^3\text{E}_{1\text{u}}$ states induced by ν_8 . The O_2 -perturbed data are compared to each other and the crystal data in Table III.

If the $^3\text{B}_{1\text{u}}$ crystal origin is assumed to be similar in energy to the unobserved $\text{O}_2/\text{C}_3\text{H}_8$ liquid perturbed $^3\text{B}_{1\text{u}}$ origin (gas to liquid and gas to crystal shifts are quite similar for C_6H_6^3), then a value of 916cm^{-1} for ν_8 can be obtained. The large difference between the pseudo Jahn Teller ν_8 frequency in the crystal and O_2 -perturbed systems may be an environmental effect. The second band, located 567cm^{-1} above the first, could be either 8_0^2 or $8_0^1 6_0^1$. A concrete determination is not possible with the present data.

Perhaps the most interesting and significant aspect of the present experiments has to do with the $O_2/C_6H_6/C_3H_8$ system itself. In these dilute cryogenic solutions, $C_6H_6:O_2:C_3H_8 = 1:10:10^4$, the statistical probability for O_2/C_6H_6 pair formation is of the order of 10^{-7} . Such a low concentration of (statistical) pairs could not possibly be responsible for the observed absorptions. It seems certain that there must be a preferential O_2/C_6H_6 interaction and that this interaction results in a decidedly non-statistical O_2/C_6H_6 "pair" formation. These pairs or clusters may be regarded as "van der Waals" molecules or clusters. We are presently studying the properties of these interesting systems in order to elucidate cluster size (1 to 1 O_2/C_6H_6 or n to 1 O_2/C_6H_6), cluster life time, cluster photochemistry, and other cluster excited and ground states. The nature of the O_2/C_6H_6 potential interaction in cryogenic liquid should prove important in the understanding of the recently reported aggregation phenomena in cryogenic liquids.^{3b}

V. CONCLUSIONS

The observation of O_2 -induced triplet transition intensity in cryogenic liquid solutions represents yet another application of such systems to the study of molecular, aggregation, and liquid state phenomena. Moreover, such mixed cryogenic liquids can provide a new data set with which to analyze the triplet states of organic molecules. In the C_6H_6 (C_6D_6)/ O_2 / C_3H_8 system, as an example, three conclusions can be reached.

1. ν_8 (e_{2g}) effectively couples the $^3B_{1u}$ and $^3E_{1u}$ states and appears to dominate the $^3B_{1u} \leftarrow ^1A_{1g}$ absorption spectrum in all environments.
2. ν_8 in the $^3B_{1u}$ state is quite sensitive to environmental perturbations: in O_2 -perturbed systems its value is $\sim 900\text{cm}^{-1}$ but in the crystal its value is $\sim 250\text{cm}^{-1}$.
3. C_6H_6 triplet state energies, in general, both $^3B_{1u}$ and $^3E_{1u}$, are sensitive to their surroundings probably because of the Jahn Teller and pseudo Jahn Teller nature of these states.

The overall triplet state intensity enhancement for C_6H_6 is associated with the formation of a van der Waals complex or molecular species in the cryogenic liquid.

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TABLE I
OBSERVED TRIPLET STATE TRANSITIONS OF C_6H_6 AND C_6D_6
IN O_2/C_3H_8 SOLUTIONS AT 87K.

Molecules	C_6H_6 (cm^{-1})		C_6D_6 (cm^{-1})	
	Frequency	Difference	Frequency	Difference
${}^3E_{1u} + {}^1A_{1g}$	36968		37067	
		587		629
	37555		37696	
${}^3B_{1u} + {}^1A_{1g}$	(29647)*			
		916		
	30563			
		562		
	31125			

*ref. 1a: crystal result, see text for explanation.

TABLE II
COMPARISON OF ${}^3E_{1u}$ ${}^1A_{1g}$ DATA FOR C_6H_6 AND C_6D_6

Molecules	Systems		O_2 -Perturbed (cm^{-1})				Crystal ⁽²⁾ (cm^{-1})	
			$O_2/C\ H$ (1)		O_2 Matrix (2)			
			Frequency	Difference	Frequency	Difference		
C_6H_6			36968		36560		36947	
				587		610		549
			37555		37170		37496	
C_6D_6			37067		36784		37147	
				629		712		
			37696		37496		---	

(1) this work

(2) ref. 2b

TABLE III
COMPARISON OF ${}^3B_{1u} + {}^1A_{1g}$ DATA FOR C_6H_6

Pure Crystal ⁽¹⁾		O_2 -Perturbed System			
Frequency(cm^{-1})	Assignments	Frequency (cm^{-1})			New Assignments
		Cryogenic Liquid ⁽²⁾	Gas Phase ⁽³⁾	Matrix ⁽⁴⁾	
29647	(0,0)	---	29516	29410	(0,0)
29886	8_0^1	30563	30500	30395	8_0^1
---	---	31125	---	---	8_0^2 or 8_0^6
30787	8_0^1	---	31300	31350	8_0^1

(1) ref. 1a

(2) this work

(3) ref. 2a

(4) ref. 2c

FIGURE CAPTIONS

Figure 1

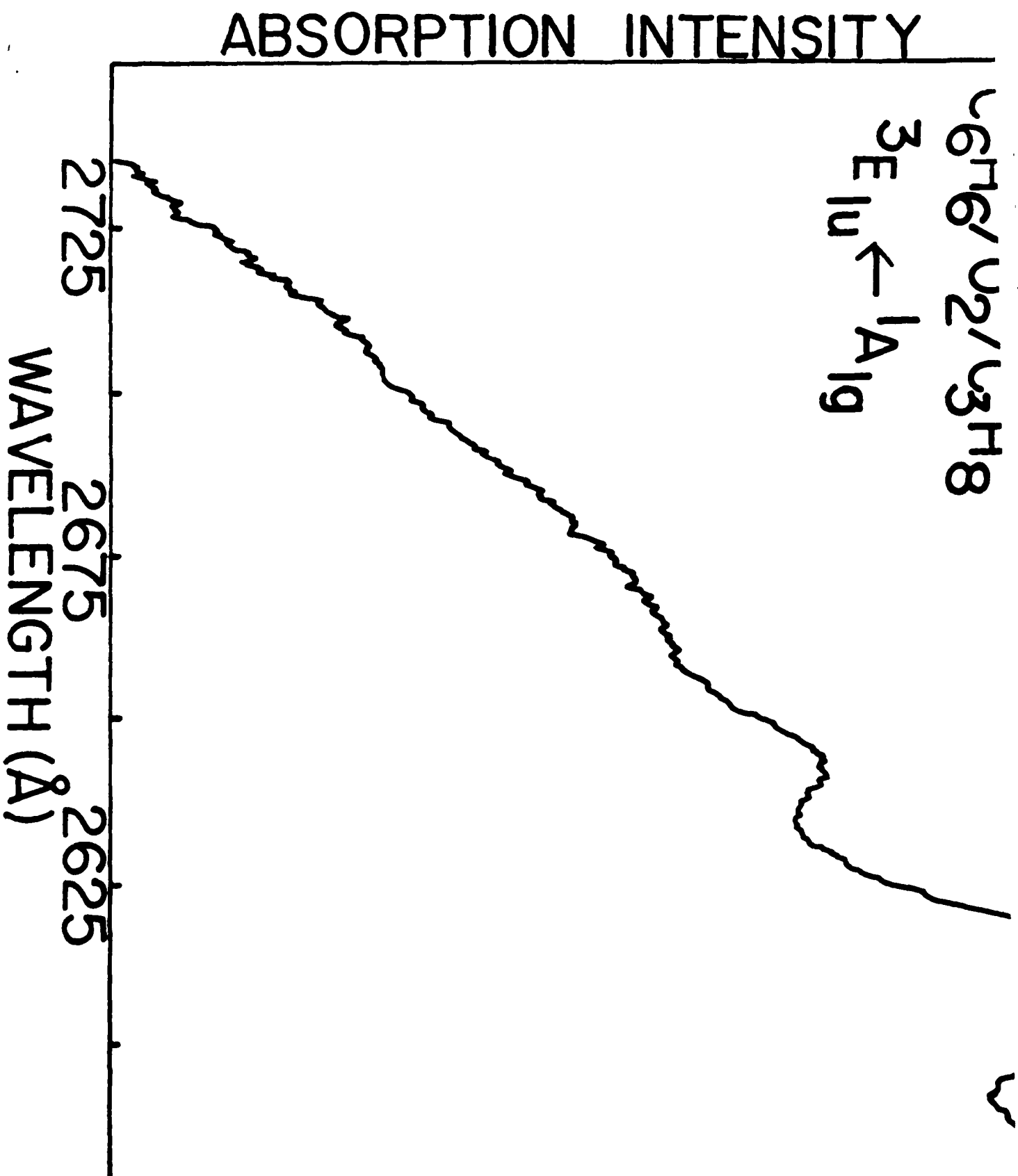
${}^3E_{1u} \leftarrow {}^1A_{1g}$ absorption of C_6H_6 in O_2 and C_3H_8 mixed solution at $87^\circ K$ ($1:10:10^4$). The features at $2642\text{\AA}$ and $2608\text{\AA}$ are the (0,0) and the 6_0^1 of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition of C_6H_6 .

Figure 2

${}^3B_{1u} \leftarrow {}^1A_{1g}$ absorption of C_6H_6 in O_2 and C_3H_8 mixed solution at $87^\circ K$ ($1:10:10^4$).

Figure 3

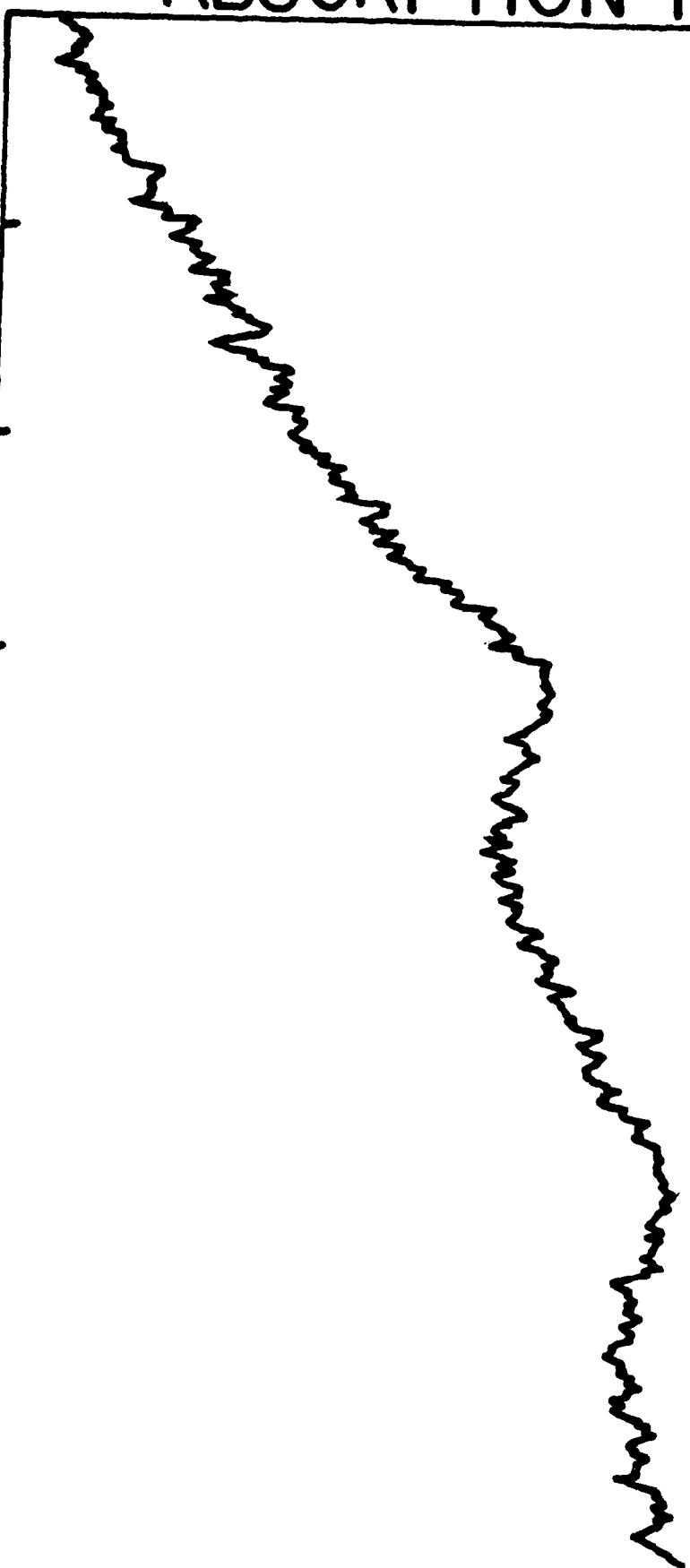
${}^3E_{1u} \leftarrow {}^1A_{1g}$ absorption of C_6D_6 in O_2 and C_3H_8 mixed solution at $87^\circ K$ ($1:10:10^4$). The feature at $2630\text{\AA}$ is the (0,0) of the ${}^1B_{2u} \leftarrow {}^1A_{1g}$ transition C_6D_6 .



U6H6/U2/C3H8

${}^3B_{1u} \leftarrow {}^1A_{1g}$

ABSORPTION INTENSITY



3325

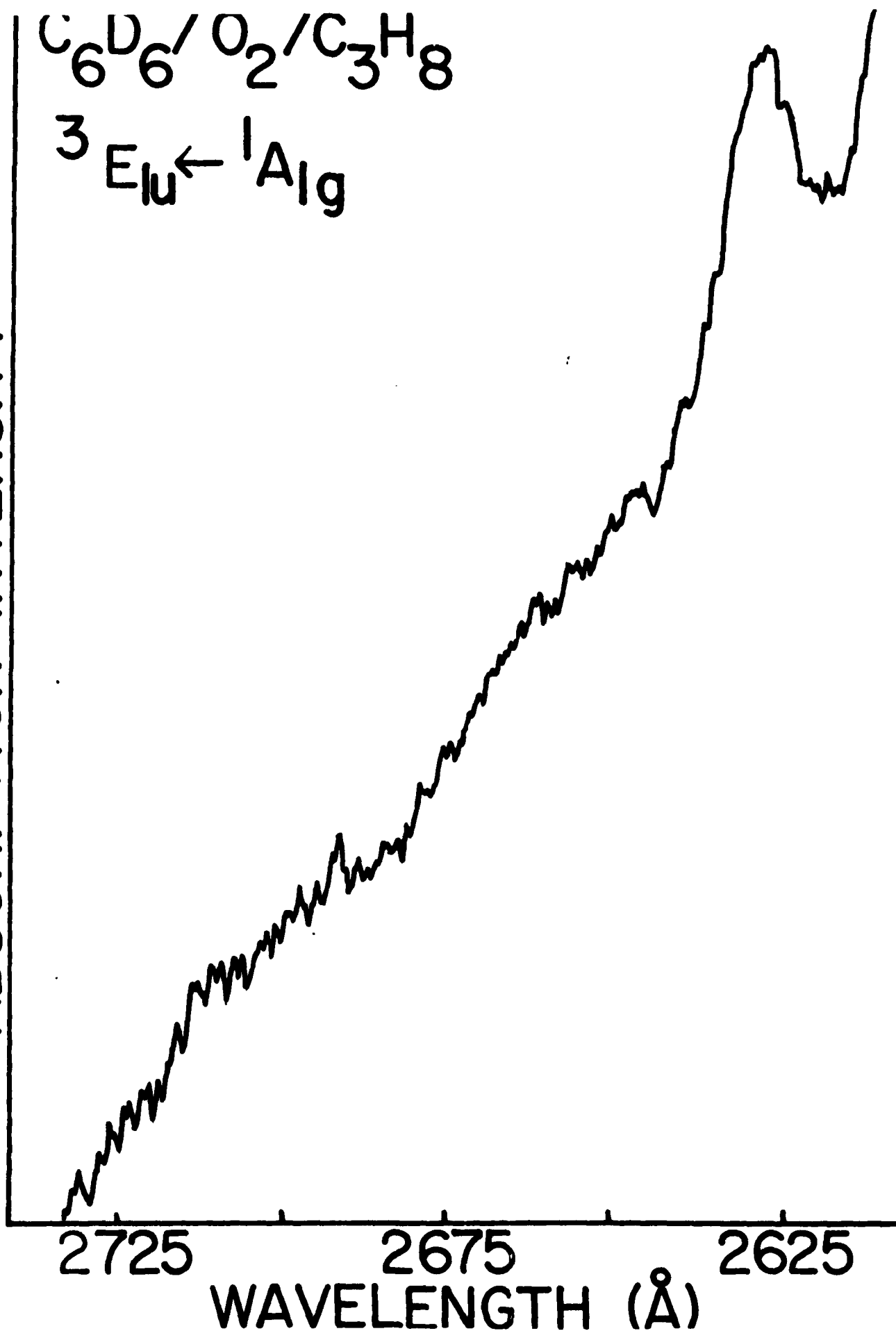
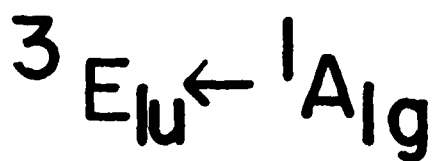
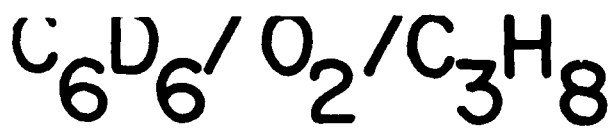
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