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may be absent in A*, or in A^+ or in both. The coupling of vibrational and rotational angular momenta[14] facilitates the slight change of rotational state needed to satisfy such restrictions when A^+ is formed from A* or vice versa. On making the usual approximation employed in a classical description of rotational partition functions the absence of certain rotational states in A* or A^+ is accounted for by letting one factor in Ω^* be $1/\sigma$ and one in Ω^+ be $1/\sigma^+$.

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[14] The total angular momentum, which is constant, has vibrational and rotational terms. [See E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 277]. The coupling of these two contributions in the kinetic-energy expression permits some interchange, the equations of motion show.

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First and Second Triplets of Solid Benzene*

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Absorption spectra have been taken of the O_2-perturbed first ($^3B_{1u}$) and second ($^3E_{1u}$) triplets of solid benzene at 4.2°K. Spectra of both C_6H_6 and C_6D_6 were obtained. The (0–0) bands of the first triplet occur at 29 674±25 cm^{-1} for C_6H_6 and 29 851±25 cm^{-1} for C_6D_6. For the second triplet they lie at 36 560 cm^{-1}±50 for C_6H_6 and 36 784±50 cm^{-1} for C_6D_6. The result for the first triplet of C_6H_6 compares very favorably with Evans' gas-phase O_2-perturbed spectrum. It is also in satisfactory agreement with Nieman's accurate phosphorescence measurements on isotopic mixed crystals of benzene which place the C_6H_6 (0, 0) band position in the crystal at 29 657.1 cm^{-1}. Many precautions were taken to eliminate the possibility of mis identification of the second triplet. The observation that the O_2-enhanced first triplet and the O_2-enhanced bands in the 36 600-cm^{-1} region always appear together and with approximately the same relative intensities is considered to be the best evidence for the assignment. However, the rather broad structure obtained by the O_2-perturbation technique does not allow all the uncertainties in the identification to be completely removed, nor does it allow a detailed study of this interesting state.

A detailed evaluation of the purity of the benzene is made, and a method is described for the preparation of material having ultrahigh spectroscopic purity. Crystals, up to 5 cm in length, of this very highly purified C_6H_6 and C_6D_6 were studied at 4.2°K to ascertain if the singlet–triplet absorptions could be seen in the absence of a perturbation. The long crystals showed some sharp and some broad ($\Delta\nu\approx150$ cm^{-1}) absorptions starting at 36 947±50 cm^{-1} in C_6H_6 and at 37 147±50 cm^{-1} in C_6D_6. The broad absorptions correlate reasonably well with the features assigned to the second triplet in the O_2-perturbation experiments. The first triplet is too weak to be observed in the long-crystal experiments. The position of the second triplet lies about 3000 cm^{-1} above that given by the Pariser–Parr calculation. This places the second triplet about nine-tenths rather than half of the distance from the lowest triplet to the lowest excited singlet.

INTRODUCTION

For many years the location of the second triplet state of benzene has been the object of much research, both theoretical and experimental.[1,2] This intense interest has been generated by theoretical predictions, many and varied, of the energies of the excited states of aromatic hydrocarbons. All theoretical predictions identify the second triplet of benzene as the orbitally degenerate $^3E_{1u}$ state, and most of these predictions place the second triplet in the experimentally accessible region between the lowest triplet and the lowest singlet.[3] Semiempirical theories[4,5] for these energy levels, which are based partially on spectral data, have seemed fairly promising. Thus it becomes of great importance to fix experimentally as many of the states of the lowest π–π^* manifold of benzene as possible. Up to now, all three singlet states, but only one triplet state, the lowest, have been identified.[6]

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* Supported in part by the U. S. Atomic Energy Commission.

† Contribution No. 3211.

[1] J. R. Platt, J. Mol. Spectry. **9**, 288 (1962).

[2] D. R. Kearns, J. Chem. Phys. **36**, 1608 (1962).

[3] J. W. Moskowitz and M. P. Barnett, J. Chem. Phys. **39**, 1557 (1963); note that the use of a Goeppert-Mayer–Sklar core, accurate integrals, and extensive configuration interaction (Column *e* of Table I in this reference) places the second triplet *above* the first singlet.

[4] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466, 767 (1953).

[5] H. E. Simmons, J. Chem. Phys. **40**, 3554 (1964).

[6] G. W. Robinson, in *Methods of Experimental Physics*, edited by D. Williams (Academic Press Inc., New York, 1962), Vol. 3, p. 244.

DETECTION OF HIGHER TRIPLETS IN AROMATIC HYDROCARBONS

Phosphorescence

The lowest triplet can be studied in emission (phosphorescence) since it can be populated by excitation into nearby singlets. The lowest triplet is the lowest excited state, and, even though the radiative transition probability for the emission process is extremely small, competing nonradiative processes are themselves sufficiently slow to allow detectable quantum yields of light emission. For higher triplets, however, nonradiative paths to lower triplets are so much more important than the highly forbidden radiative process back to the ground singlet state that quantum yields are vanishingly small.

Triplet–Triplet Absorption

Triplet–triplet absorption from the long-lived, lowest triplet state of benzene could yield information about higher triplets, just as it has done in other aromatic hydrocarbons.[7] However, $g\leftrightarrow u$ selection rules would not allow strong absorption into the nearby higher triplets since these have the same parity as the lowest triplet. This selection rule is weakened if the molecule distorts and its center of symmetry is lost. The distortion may occur through molecular vibrations, solvent effects, or simply because the equilibrium configuration for the triplet *is* distorted. In any case the transition is not expected to be strong. This fact combined with the inconveniently low energy of the transition would cause detection of the second triplet in benzene by this technique to be difficult. Actually no evidence has yet been obtained for any kind of triplet–triplet absorption in benzene.[8]

Heavy-Atom Perturbations

Passing over phosphorescence and triplet–triplet absorption, there remain three other experimental methods which can be used to study the second triplet state of benzene: heavy-atom perturbation, O_2 perturbation, and direct unperturbed absorption studies. Heavy-atom perturbations can arise from the environment or from substituents. Assuming the theoretical ideas of Robinson[9] concerning environmental heavy-atom perturbations to be correct, perturbed oscillator strengths of not much more than $f\approx 10^{-7}$ may be obtained from solvent perturbations.[10] If the heavy atom is chemically substituted onto the benzene ring, much larger oscillator strengths may result.[11] Even though future work may concern pure-crystal studies at 4.2°K of benzenes containing heavy-atom substituents, the primary interest in this paper revolves about the second triplet of benzene itself or of externally perturbed benzene.

Unperturbed Absorption

The experimental value of the oscillator strength for the spin and orbitally forbidden transition ${}^3B_{1u}\leftrightarrow{}^1A_{1g}$ (the first triplet) is $f\approx 10^{-10}$. This value has been derived from phosphorescence-lifetime measurements[9,12] on both C_6H_6 and C_6D_6 combined with the accurate quantum-yield results of Lim.[13] Purely theoretical values[14] of 10^{-9}–10^{-10} for the oscillator strength of the spin-forbidden but orbitally allowed second-triplet transition therefore seem too small. Such calculations may be plagued by cancellation effects in the spin–orbit energy of aromatics,[15] in which case small wavefunction

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[7] G. Porter and M. W. Windsor, Proc. Roy. Soc. (London) **A245**, 238 (1958).

[8] The most favorable system in which to search for the triplet–triplet absorption is probably the C_6D_6–argon system at 4.2°K. Here a gaseous mixture of less than 1% C_6D_6 with argon is condensed on a liquid-helium-cooled surface. The ${}^3B_{1u}$ lifetime in this system is nearly 30 sec, and all observed vibronic components are quite sharp. The study in our laboratory of this system using intense, steady illumination for triplet excitation plus a continuum for detection of triplet–triplet absorption showed negative results for the region 2650–7000 Å. In contrast, using the same technique for naphthalene, the ${}^3B_{1u}\leftarrow{}^3B_{2u}$ absorption in the 4000-Å region could be detected routinely with much greater intensity than that of the 3200-Å ${}^1B_{3u}\leftarrow{}^1A_{1g}$ absorption even though the latter transition involves the ground state! No attempt was made to search for the ${}^3E_{1u}\leftarrow{}^3B_{1u}$ transition of benzene which, according to results presented in this paper, should have its origin near 1.5μ.

[9] G. W. Robinson, J. Mol. Spectry. **6**, 58 (1961).

[10] See Ref. 9, pp. 71–77. It is envisioned that the heavy-atom enhancement is caused by weak exchange interactions that couple the triplet state of the molecule to a Russell–Saunders triplet component of the electronically excited heavy-atom perturber. The triplet component of the perturber is in turn coupled to the singlet component of the perturber through strong spin–orbit mixing. In this manner the triplet state of the perturbed molecule borrows some singlet character from the perturber. For heavy-rare-gas perturbations, second-order perturbation theory yields,

$$f_p=[z\delta^2\zeta^2/2(F_0-\bar{E}_T)^4]\ (\bar{E}_T/F_0)f_r$$

for the perturbed oscillator strength caused by the lowest ${}^3P_1$, ${}^1P_1$ pair of the rare gas. Here z is the coordination number of solvent atoms around the perturbed molecule, δ is the electrostatic "excitation transfer" matrix element which is of the exchange type, ζ is the spin–orbit coupling constant for the ${}^1P_1$ and ${}^3P_1$ states of the rare gas, F_0 is the term value for the rare gas, $\bar{E}_T$ is the average triplet-state energy of the perturbed molecule, and f_r is the oscillator strength for the rare gas. A summation of such terms should be made over all perturbing states. For the most effective rare-gas perturber, solid xenon, the observed f_p for benzene is roughly 2.5×10^{-8} compared with the unperturbed value $f\approx 10^{-10}$. Here $z\approx 10$, $\delta\approx 50\ \text{cm}^{-1}$, $\zeta=-6086\ \text{cm}^{-1}$, $F_0=71\,095\ \text{cm}^{-1}$, and $\bar{E}_T\approx 29\,800$ (see Table II of Ref. 9). Neglecting other states as a first crude approximation, a rare-gas ${}^1P_1\leftarrow{}^1S_0$ oscillator strength of $f_r\approx 0.4$ would be required to explain the experimental result. This is a very reasonable value for f_r. To find a "clean" perturber which would push the perturbed oscillator strength to a factor of, say, more than 100 of what it is in xenon, would be difficult.

[11] A chemically bound heavy-atom substituent is expected to yield a δ which is 10–100 times larger than that for an intermolecularly bound entity.

[12] M. R. Wright, R. P. Frosch, and G. W. Robinson, J. Chem. Phys. **33**, 934 (1960).

[13] E. C. Lim, J. Chem. Phys. **36**, 3497 (1962).

[14] E. Clementi, J. Mol. Spectry. **6**, 497 (1961).

[15] D. S. McClure, J. Chem. Phys. **20**, 682 (1952). Deviation of the molecular eigenfunction from a $2p$ (carbon) representation in the D_{6h} molecule or in a distorted form of the molecule would cause the cancellation to be inexact.

errors would give rise to serious errors in the oscillator strengths. Semiempirical estimates can, however, be made and are probably more reliable. For example, assume that the primary singlet–triplet mixing mechanism is spin–orbit coupling between $^1E_{1u}$ and $^3E_{1u}$ with further vibronic coupling between $^3E_{1u}$ and $^3B_{1u}$.[16] The vibronic coupling constants for benzene singlets can be computed from the observed oscillator strengths and excitation energies for the $^1E_{1u}$, $^1B_{1u}$, $^1B_{2u}\leftarrow{}^1A_{1g}$ transitions.[6] One obtains $\langle {}^1E_{1u} \mid {}^1B_{1u}\rangle \approx 2000$ cm^{-1} and $\langle {}^1E_1 \mid {}^1B_{2u}\rangle \approx 800$ cm^{-1}. Assuming the same kind of values hold in the triplet manifold and taking the energy separation between the $^3B_{1u}$ and $^3E_{1u}$ states to be roughly 7000 cm^{-1}, one finds that absorption into the $^3E_{1u}$ state should be from 12–75 times more intense than absorption into the $^3B_{1u}$ state.

It has been estimated that well over a meter of path length of liquid benzene would be required for the detection of the unperturbed first triplet transition.[9] According to the above semiempirical estimate, the $^3E_{1u}\leftarrow{}^1A_{1g}$ transition would presumably require 12–75 times less path, providing the line breadths were comparable. In such long paths of benzene, impurity absorption and hot-band structure from nearby intense singlet–singlet transitions become dominant. The hot-band structure is an especially severe problem when searching for the second triplet of benzene, since this state lies virtually in the shadow of the first singlet. The hot-band structure can be eliminated completely by working at liquid-helium temperatures.

The sharpening of structure is an added bonus at these low temperatures. Spectral line sharpening increases the chance of observing weak transitions. For instance, consider the oscillator strength for a transition

$$f=4.3\times10^{-9}\int\epsilon_\nu d\nu, \tag{1}$$

where the integration is carried out over the extinction coefficient for all vibronic components, the units of ν being cm^{-1}. Taking a Gaussian line shape for each of m vibronic components, assumed for simplicity all to have equal intensity, one has[6]

$$f=(4.3\times10^{-9})(m)(1.06\epsilon_{\max}\Delta\nu_{\frac{1}{2}}), \tag{2}$$

where $\Delta\nu_{\frac{1}{2}}$ is the width (in cm^{-1}) at half-maximum of each component, and $\epsilon_{\max}$ is the extinction coefficient at maximum absorption. If half of the incident light is absorbed at the maximum extinction, detection of the absorption is well above threshold. In that case the required path length in centimeters is given by,

$$l(\text{cm})=1.4\times10^{-9}(m\Delta\nu_{\frac{1}{2}}/Cf), \tag{3}$$

where C is the concentration of the absorber in moles per liter.

There are about five intense components in the benzene $^1B_{2u}\leftarrow{}^1A_{1g}$ absorption spectrum. Assume the same holds true for the triplets; thus $m\approx5$. In pure crystalline benzene $C\approx12$, and for the benzene transitions thus far observed at 4.2°K, the narrowest absorptions have $\Delta\nu_{\frac{1}{2}}\approx2\pm1$ cm^{-1}. This means that a path length of about 5–20 cm would be necessary to give $(I/I_0)_{\max}=0.5$ for absorption into the first triplet providing the absorption components were sharp. At room temperature in the liquid, the $\Delta\nu_{\frac{1}{2}}$ of each of the five most intense components is around 500 cm^{-1}, and Eq. (3) yields a path length of 30 m.[17] This simple estimate illustrates the great advantages of working at low temperatures where the lines are of minimum width. For the second triplet, as noted earlier, one expects an increase of around one to two orders of magnitude in the oscillator strength compared with that of the first triplet. Thus it would seem to be a relatively easy matter to detect the second triplet in long-path absorption at low temperatures. It will be seen, however, that line broadening substantially lessens the ease with which the absorption can be detected.

O_2 Enhancement

In our initial search for the second triplet state of benzene, the method of O_2 enhancement[18] was decided upon because of the extremely small oscillator strengths for unperturbed, multiplicity-forbidden transitions in aromatic hydrocarbons. In the present work, the O_2-perturbation method has been extended to low temperature in order to sharpen structure and to remove hot-band interference from the nearby $^1B_{2u}$ state. A perturbed oscillator strength of 10^{-5} would allow detection of the triplets in 0.01-cm paths of solid benzene even though the respective $\Delta\nu_{\frac{1}{2}}$ were as broad as 150 cm^{-1}. Such paths lengths can easily be obtained through deposition techniques.[9] The O_2-perturbation method, while yielding broad absorption lines and inaccurate vibrational spacings, would fix, within experimental accuracy, the position of the (0–0) band for the high triplets of aromatic hydrocarbons.

EXPERIMENTAL

Purification of Benzene

In the study of emission spectra or weak absorption spectra of organic molecules, the question of chemical

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[16] A. C. Albrecht, J. Chem. Phys. **33**, 156, 169 (1960); **38**, 354 (1963).

[17] An earlier estimate of 1.5 m by Robinson, Ref. 5, was based on a detection threshold suggested by Craig *et al.*, J. Chem. Phys. **29**, 974 (1958). It is felt that for the broad spectra, on top of a rapidly rising background absorption, such a threshold is unrealistic. The 30-m value above, it should be stressed, is not a threshold value. It is the path at which $(I/I_0)_{max}=0.5$.

[18] D. F. Evans, J. Chem. Soc. **1957**, 1351

purity must always be carefully considered. For this reason a section devoted to the benzene purification methods used in this work seems appropriate.

Sources of the raw starting material were as follows. The C_6H_6 was obtained from three different sources: from the Phillips Petroleum Company, from D. R. Davis of the Chemistry Department, UCLA, and from the National Bureau of Standards. Two different samples of Phillips research-grade benzene were employed, one sample stated to have 99.93 mole % purity and another reportedly being 99.89 mole % pure. This material is furnished in capped bottles and is therefore air contaminated. It is stated that toluene is the major impurity, but it has been reported that about half of the impurity is water.[19] The sample from UCLA had been twice purified by vapor-phase chromatography, degassed, and vacuum sublimed into a tube which was then sealed under vacuum. The NBS sample was prepared by carrying out a large number of careful recrystallizations using the Phillips research-grade benzene as starting material. Freezing-point data were used to set the purity level of the NBS benzene at 99.999 mole %.

Long-crystal absorption spectra provide a sensitive test for spectroscopic impurities, i.e., those impurities which alter the absorption or emission spectrum of an otherwise pure material. If the absorption spectrum of the contaminant is sharp, and its oscillator strength is high, impurity levels in the 10^{-7}–10^{-10}-mole fraction range can be detected in a 5-cm path of crystalline benzene.[20] Because of extensive impurity absorption, in none of the three types of raw starting material mentioned above was it possible to get sufficient radiation through a 5-cm crystal to study absorption in the 2650–2800-Å region! A series of experiments on 2-cm crystals was therefore carried out to determine the nature of these contaminants. The UCLA sample was by far the most inferior, showing strong, broad absorption well to the long wavelength side of 3000 Å, and perhaps indicating the inadequacy of VPC purification for the removal of trace impurities. The major spectroscopic impurity in both the NBS sample and the Phillips sample was found to be phenol. An estimate made from absorption intensity indicated that the NBS sample contained 10^{-5} parts of phenol and little else that was spectroscopically observable. Interestingly enough, the Phillips research-grade benzene showed the smallest amount of impurity absorption. However, a wide variety of chemical impurities seemed to be present in the Phillips samples. Again, the major spectroscopic impurity was phenol, but it was present to only about $\frac{1}{3}$ the extent of that in the NBS sample. A broad absorption band near 2690 Å is perhaps due to monochlorobenzene, while an underlying, nearly continuous absorption might be caused by toluene plus other unidentified impurities in the mole-fraction range 10^{-5}–10^{-6}.

The C_6D_6 was obtained from Merck, Sharp & Dohme, of Canada, Ltd. It was said to be 99.5 at. % isotopically pure. The chemical purity was much like that of the NBS C_6H_6 sample, showing a mole fraction of about 10^{-5} perdeuterophenol as the major spectroscopic impurity.

The occurrence of phenol as a trace impurity in benzene has been noted previously.[21] Its wide occurrence suggests that benzene may react with O_2 from the atmosphere. The reaction must be autoinhibited, however, since large amounts of phenol never seem to be produced. Care must therefore be exercised when handling high-purity benzene, just as it must be for higher aromatic homologs, so as not to allow atmospheric contamination.

It should be stressed that impurities at the concentration levels existing in the Phillips research-grade or NBS C_6H_6, or the Merck C_6D_6 caused no problems for sample thicknesses up to about 0.2 mm. That is, in the absence of O_2, only extremely weak impurity absorption could be detected in such samples at wavelengths through the near ultraviolet all the way down to the benzene cutoff at 2650 Å. Certain spectra appeared when 2% O_2 was present. They are discussed more fully later on.

For spectroscopic investigation of 5-cm benzene crystals much better purity is required than exhibited by any of the "raw starting materials." The benzene used in the long-crystal experiments is purified in the following manner. From the beginning of the process until after the crystal is grown, the benzene is kept in a vacuum system. A schematic diagram of the apparatus is shown in Fig. 1. The vacuum system is isolated from the oil diffusion and mechanical pumps by a $\frac{1}{2}$-in. Kerotest metal valve (a) having a Teflon gasket. The benzene is transferred from a breakseal tube (b) to a vessel (c) where it is dried over vacuum distilled potassium. It is then degassed and transferred by two vacuum distillations through (e_1) to a vessel (i) mirrored with vacuum-distilled high-purity cesium (j). After the initial reaction, the sample is degassed and the cesium reaction vessel is sealed off at the constriction (f_5) from the rest of the vacuum system. The benzene is then refluxed over the cesium at about 100°C for 1 h. Conditions very much more severe than these were found to degrade the benzene and produce a large amount of undesirable impurity absorption. During the cesium refluxing, the parts of the system previously used are "pulled off" under vacuum at the constrictions (f_1), (f_2), and (f_3). The remainder of the

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[19] International Union of Pure and Applied Chemistry, Commission on Physico-Chemical Data and Standards, "Cooperative Determination of Purity by Thermal Methods," Report of the Organizing Committee, July 14, 1961, Vol. I.

[20] For example, 0.1% phenol can easily be detected as an impurity in a 10-μ-thick crystal of benzene. For a 5-cm crystal, which is 5000 times thicker, 2×10^{-7} parts of phenol would be easily detected. The oscillator strength of the phenol transition is roughly 0.03.

[21] V. L. Broude, Soviet Phys.—Uspekhi **4**, 584 (1962) [Usp. Fiz. Nauk **74**, 577 (1961)].

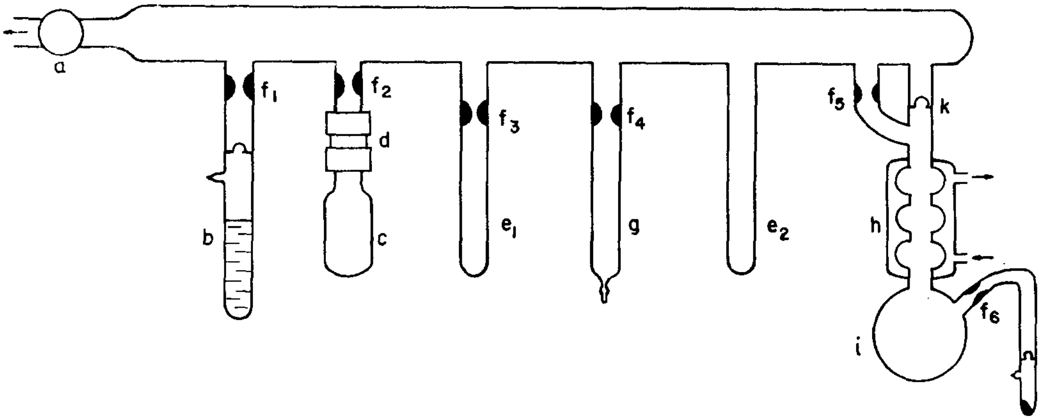

FIG. 1. Benzene purification manifold. (a) Kerotest (Kerotest, Inc., Pittsburgh, Pennsylvania) metal valve to cold traps, gauges, and oil-diffusion pump. (b) Benzene to be purified. (c) Potassium mirrored drying vessel. (d) Swagelok union, ½ in., (Crawford Fitting Company, Cleveland, Ohio) for adding potassium. (e) Receiving vessel for primary vacuum distillations. (f) Constrictions for pulling off under vacuum. (g) Bridgman crystal-growing tube (14 mm×10 cm). (h) Water-cooled condenser. (i) Cesium reflux vessel (~30 cc). (j) Cesium. (k) Breakseal.

system is thoroughly flamed until the limiting vacuum of 2×10^{-6} mm of Hg is attained. By means of a breakseal (k), the cesium vessel is reopened to the main vacuum manifold. The benzene is degassed thoroughly, and by two vacuum distillations through the intermediate tube (e_2) it is transferred into a Bridgman crystal-growing tube (g).[22] It is then cooled to liquid-nitrogen temperature, and the tube is pulled off at (f_4). A 5-cm crystal purified in this way showed little or no absorption throughout the ultraviolet down to the 2700-Å region. In particular the mole fraction of phenol was estimated to be less than 10^{-8}!

Benzene–O_2 Experiments

The central idea here is to observe the spectrum of a mixture of benzene and oxygen in the region just to the long-wavelength side of the singlet–singlet system (${}^1B_{1u}\leftarrow{}^1A_{1g}$; $f\approx0.0014$) whose origin lies near 2650 Å. Since thin (<0.2-mm) samples are used, purity is not a problem for the O_2-perturbed experiments. Phillips research-grade benzene, degassed but without further purification, was therefore used for these experiments.

As mentioned earlier, low temperatures are required to eliminate hot-band structure associated with the relatively much stronger singlet–singlet system.[23] Liquid-helium temperature is used in all of the experiments reported here. Another advantage of low temperatures, the sharpening of band structure, is not realized to its fullest extent in the O_2-perturbation experiments.

Because of the broad structure, a spectrograph of relatively low resolution is adequate for this portion of the work. The instrument used was a Bausch & Lomb medium quartz prism spectrograph. A 150-W Xe lamp was used as source for the absorption studies, while a Bausch & Lomb *f*/3.5 grating monochromator, in conjunction with the Xe lamp, was used to excite emission. Combinations of bromine gas, Corning Glass #9863, and aqueous nickel sulfate filters were used to reduce stray light from longer wavelength radiation.

Some earlier experiments in our laboratory attempted to detect the second triplet state of benzene by depositing at liquid-helium temperature benzene with excess oxygen; i.e., benzene in an oxygen "matrix." Only the well-known visible and near-ultraviolet bands of condensed oxygen[24] were discernible. Besides, in oxygen-rich systems it is very difficult, because of scattering, to get light through the thick deposits necessary for such low concentrations of benzene.

To avoid the problem of O_2 absorption which is caused by O_2–O_2 interactions and simultaneously to increase the path length of benzene, a mixture rich in benzene containing a few percent O_2 was used. In order for most of the benzene molecules in the solid to have nearest-neighbor contact with at least one oxygen molecule, an optimum concentration of oxygen would lie perhaps in the 5%–10% range. However, the maximum amount which was actually used was 2%, since higher concentrations seem to give deposits which strongly scatter the light.

The gaseous mixture containing 98% benzene and 2% oxygen was deposited on a window cooled to liquid-

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[22] D. Fox, M. M. Labes, and A. Weissburger, *Physics and Chemistry of the Organic Solid State* (Interscience, Publishers Inc., New York, 1963) p. 267.

[23] For example, according to this paper, the separation of the unperturbed (0, 0) bands of the first singlet and the second triplet is only about 900 cm^{-1}. At room temperature, hot-band structure from the first singlet in the vicinity of the (0, 0) band of the second triplet is therefore expected to be down in intensity by only a factor of 150. Since even under O_2 perturbation the second triplet is at least 100 times weaker than the first singlet, there would be no chance whatsoever of detecting the second triplet at room temperature. The very highest temperature at which one can expect to separate the second triplet from the hot-band structure of the first singlet is 100°K, and much lower temperatures are to be preferred.

[24] L. J. Schoen and H. P. Broida, J. Chem. Phys. **32**, 1184 (1960).

TABLE I. First and second triplet-state energies (in cm^{-1}) of C_6H_6 and C_6D_6 in O_2-perturbed systems and pure crystals.

	O_2 perturbed		Benzene crystals	
	C_6H_6[a]	C_6D_6	C_6H_6	C_6D_6
$^3B_{1u}$	29 674±25	29 851±25	29 657.1[b]	29 855.1[c]
	30 581	30 628		
	31 446	31 446		
	32 258	32 362		
$^3E_{1u}$	36 560±50	36 784±50	36 947±50	37 147±50
	37 170	37 495	37 496	not identified

[a] Evans'[18] values in the gas phase for this system are 29 440, 30 350, 31 250, and 32 100 cm^{-1}.

[b] G. C. Nieman, Ph.D. thesis, California Institute of Technology, 1965, observed in 1% C_6H_6 in 99% C_6H_6 mixed-crystal phosphorescence. The corresponding value of the (0, 0) band position for the $^1B_{2u}\rightarrow{}^1A_{1g}$ transition is 37 855 cm^{-1}. It should be noted that the pure-crystal value would be lower by about 50 cm^{-1} [see G. C. Nieman and C. W. Robinson, J. Chem. Phys. **39**, 1298 (1963)].

[c] Obtained from C_6H_6 value by adding 198 cm^{-1} [see Ref. (b)].

helium temperature in a manner similar to that described by Robinson.[9] Because of light scattering, the maximum deposit thicknesses that could be used were somewhere around 200 μ. This value was estimated from absorption intensities of the singlet–singlet systems of pure benzene and of a phenol-in-benzene standard sample. It is known that when pure benzene is deposited from the vapor phase at 4.2°K, the electronic spectrum appears very broad compared with the spectrum of a crystal of benzene more carefully prepared. It was discovered that benzene deposited at liquid-nitrogen temperature and then cooled to 4.2°K shows a sharp spectrum, just as in the case of a good crystal. Unfortunately, attempts revealed that little oxygen could be trapped in the benzene under these conditions. Furthermore, strong fluorescence emission from crystalline regions in this deposit masked any weak absorption bands which otherwise might have appeared. Therefore, this technique was abandoned in favor of the 4.2°K deposition experiments. No fluorescence occurred from the 4.2°K depositions containing O_2. Perhaps deposit temperatures intermediate between 4.2° and 77°K would have been optimum, but no attempt was made to check this point.

Long-Crystal Experiments

Thick crystals of benzene are prepared in the following manner. The crystal-growing tube containing the ultrapure benzene is lowered into a −20°C cold room through a temperature gradient of 30°C/in. at a rate of ⅛th in./h. The over-all temperature differential is about 50°C. The crystal is removed from the growing tube and both ends are cut off with a hot wire. The crystal is then polished with a warm brass block and the 5-cm sample is placed in a loosely fitting Teflon holder, the crystal being kept in an inert atmosphere during all these manipulations. At this stage the crystal is completely transparent with only minor imperfections. During radiation cooling in two stages, first to 77°K, then to 4.2°K, the crystals become somewhat cracked. However, they remain fairly translucent in spite of this difficulty.

All spectra are taken at 4.2°K with the sample in a horizontal position. The optical arrangement and light sources were the same as before. However, a 2-m grating spectrograph having a resolution of about 35 000 was utilized in place of the low-resolution prism instrument in the event that sharp structure, such as factor-group structure, exists in the $^3E_{1u}\leftarrow{}^1A_{1g}$ transition in the crystal.

IDENTIFICATION OF SECOND-TRIPLET ABSORPTION

There are three major problems in determining a weak absorption such as the second triplet of benzene. The absorption can be due to an impurity; a photoproduct can be produced during the experiment; or there can be broad but structured emission whose inverse may appear to be weak absorption. The experimental procedure is aimed at the elimination of these possibilities.

Benzene–O_2 System

The benzene-O_2 mixtures were prepared in the manner described in a previous section. A summary of absorption spectra obtained from these mixtures is presented in Table I. It is gratifying that the first triplet ($^3B_{1u}$) is easily detected by this technique. In addition to the first-triplet bands, two broad (~300-cm^{-1}) features in the 36 600-cm^{-1} region of the spectrum occur under O_2 perturbation. Microdensitometer

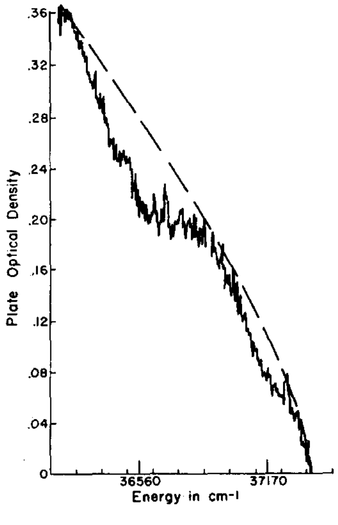

FIG. 2. Densitometer tracing of O_2-perturbed second triplet of benzene; – – – –, assumed base line.

tracings of these features are depicted in Fig. 2. It is these features which are attributed to the second triplet ($^3E_{1u}$). No absorption except that assigned to the first- and second-triplet bands occurs for wavelengths longer than the benzene first-singlet cutoff near 2650 Å.

After first observing the absorption thought to be caused by the second triplet, the system was completely taken apart and cleaned, and the experiment was repeated in the clean system. The absorption appeared as before. Then a completely different deposit Dewar (one previously used only for NH_3, ND_3, NH_2D, etc., and HCl and DCl) was used with an entirely new glass manifold. Again the same results were obtained.

To check for an impurity in the benzene, **two** different sources of C_6H_6, the Phillips and the NBS, and one sample of C_6D_6, the Merck, were tried, all giving consistent, corroborating results. An absorption spectrum of 1% phenol in C_6H_6 was taken, the second-triplet absorption was compared with this, and the two were found to be entirely different.

Spraying on benzene without O_2 *showed absolutely no absorption for* $\lambda > 2650$ *Å. This fact combined with the simultaneous observation, when* O_2 *is added, of the well-known first-triplet absorption and the 36 600-cm*$^{-1}$ *bands provides fairly convincing evidence for the existence of the second triplet in the 36 600-cm*$^{-1}$ *region.*

Three different supplies of O_2 were used; two types of Linde high-purity O_2 and an O_2 of standard purity. No evidence for the absorption spectrum of condensed O_2 was found.

The possibility of a photoproduct being formed during the experiment was also explored. Plates were taken of the O_2–benzene mixtures after sample exposure times of from less than 1 sec to 1 h using a 150-W Xe lamp, and the absorption intensity was not seen to increase or decrease. No new absorptions were produced. Furthermore, varying the light intensity over a rather wide range by means of filters and a monochromator, showed no detectable change in the observed absorptions. This fact indicates that the absorptions are not caused by transitory photoproducts. The possibility that the absorption is an artifact due to broad emission was eliminated by using a Bausch & Lomb $f/3.5$ grating monochromator with a 150-W Xe source. Fluorescence spectra using 252-mμ exciting light (bandpass of 200 Å) from this monochromator were searched for. In a $\frac{1}{2}$-h exposure, no emission in the region of interest was observed. Typical absorption exposure times are of the order of 1 sec, so we have convinced ourselves that neither photoproducts nor stray emission can account for the 36 600-cm^{-1} bands.

Based on deposit times and bandwidths, it is possible to determine the relative perturbed intensities of the two triplet states. Our estimates give

$$I(^3E_{1u}):I(^3B_{1u})\approx 10\text{–}100 \qquad (O_2 \text{ perturbed}).$$

It is interesting, and perhaps even surprising, that the ratio of the perturbed intensities is so similar to that expected on the basis of our earlier semiempirical estimates for the unperturbed intensities.

Crystalline-Benzene Experiments

As mentioned earlier, impurities are of much more concern in this system than in the previous one because of the long path length required for detection of the weak, unperturbed singlet–triplet absorption. It can be estimated that a sharp-lined impurity absorption with an oscillator strength of $f\approx 0.1$–1.0 could be detected for an impurity concentration of 1 part in 10^{10}! For this reason, a positive assignment of an absorption caused by the $^3E_{1u}\leftarrow{}^1A_{1g}$ transition without a knowledge of detailed vibronic structure in the spectrum or without the O_2-perturbation results would be impossible. Since the $^3E_{1u}$ state is so close to the relatively strong $^1B_{2u}$ state, little vibronic structure can be observed. Thus one must rely on a correspondence between any observed bands and the O_2-perturbed spectrum.

Several absorptions, some sharp and some broad, were observed in the 2650-to-2800-Å region in both C_6H_6 and C_6D_6. However, only two broad absorption features could be consistently identified in both samples, considering the expected perdeutero shift of about 200 cm^{-1} to higher energy. The intensity of these two features has always been observed to follow, in an expected manner, any changes in benzene path length. Furthermore, the intensity of these bands was found not to be dependent on the extent of purification of the sample, while the intensity of impurity lines change according to the purification method used. The most extensive purification was obtained with cesium refluxing, as described earlier in this paper. For one 5-cm crystal of C_6H_6 so purified, all impurity absorption was reduced to below or barely above the level of detection, while the two broad absorptions showed the same intensity as in less well purified samples.

The broad absorptions, which appear to belong to benzene itself, lie at 36 947±50 cm^{-1}, and 37 496±50 cm^{-1} in C_6H_6, and at 37 147±50 cm^{-1} in C_6D_6. The second absorption feature in C_6D_6 was obviously present but was strongly overlapped by a series of sharp impurity lines and was therefore difficult to measure. The impurity was perhaps an isotopic or a chemical impurity that was not completely removed by the purification technique.

The broadness of the absorption was disappointing and somewhat unexpected at first, considering the sharpness of emission and absorption lines in other crystalline-benzene transitions. After a little reflection, however, one can find many mechanisms that could broaden the $^3E_{1u}\leftarrow{}^1A_{1g}$ transition. For instance, it is certain that the orbital degeneracy of the $^3E_{1u}$ state is removed by the crystalline field whose symmetry is only C_i. (This effect may be called *electronic site-group splitting.*) Further contributions to the degeneracy removal from the Jahn–Teller effect may also be important. The removal of this twofold degeneracy on top of the expected 100–200 cm^{-1} factor-group splitting[25] divides the (0–0) band and other totally symmetric vibronic bands into eight components, transitions to six of which are allowed. It is noteworthy that the observed 150-cm^{-1} total breadth of each band is of reasonable magnitude on the basis of such contributions. Further line-broadening mechanisms must be postulated, however, in order to explain the complete lack of resolution of any of this fine structure, since, ordinarily, individual components are not more than about 5–10 cm^{-1} broad, and the instrumental resolving power of the 2-m spectrograph used is not a limiting factor. The nature of this extra broadening is not known at the present time, but crystal strain to which the site-group splitting is sensitive may be responsible.

Estimating from the plates that $(I_0/I)_{\max}$ for the second-triplet absorption bands is about 1.3 and applying Eq. (2) yields an oscillator strength of

$$f({}^3E_{1u}\leftarrow{}^1A_{1g})\approx 7\times 10^{-9} \qquad \text{(unperturbed)}.$$

It has been assumed that $\Delta\nu_{\frac{1}{2}}\approx 150$ cm^{-1} and that $m=5$, but that three of the bands are overlapped by the singlet. The oscillator strength so obtained is wholly reasonable.

In all fairness it must be pointed out that the absorptions observed in the long-crystal experiments, in spite of all our precautions, could still be due to impurities. If this were the case, one would have to conclude that either the oscillator strength and breadth of the ${}^3E_{1u}\leftarrow{}^1A_{1g}$ bands are such that the absorption could not be observed in crystals of this length, or that the transition energy lies above that of the first excited singlet. However, the correlation between the long-crystal absorptions and the O_2-perturbed bands makes the second-triplet identification plausible. The ${}^3B_{1u}$ state was never observed in these long crystals. This fact is consistent with the oscillator strength $f\approx 10^{-10}$ for this transition.

SUMMARY

The following constitutes a summary of the reasons that the absorption bands in C_6H_6 and C_6D_6, whose origins lie, respectively, at 36 560 and 36 784 cm^{-1} in the O_2-perturbed system and at 36 947 and 37 147 cm^{-1} in the pure crystals, are believed to belong to the second-triplet (${}^3E_{1u}$) transitions in these molecules.

(1) Evidence that the bands are not caused by impurity absorptions.

(a) The bands in C_6D_6 are shifted 220±50 cm^{-1} to higher energy from those in C_6H_6. The size of the shift compares reasonably well, considering the accuracy of the measurements, with the deuterium shift in the other benzene transitions. This is not a binding argument, however, since protonated vs deuterated chemical impurities may well behave in the same manner.

(b) The absorption was seen in two sources of C_6H_6 and a totally different source of C_6D_6.

(c) Varying the source of O_2 produced no effect.

(d) *Except for the 5-cm crystals, the absorption is not seen without O_2 in the sample.* This is the case not only for a deposited sample but also for a 2-cm-thick crystal of C_6H_6 or C_6D_6.

(e) After making various checks, the sample used in the O_2-perturbation experiments was found to be much too thin to show impurity absorption from C_6H_6, C_6D_6, or O_2.

(f) The O_2-perturbed absorption was seen in two entirely different deposit systems.

(g) Varying the exposure time and the light intensity produced no change whatever in the observed spectra, indicating that photoproducts are not responsible for the absorption.

(2) After careful investigation, the possibility was eliminated that the weak, broad absorption is an artifact caused by the presence of broad emission.

(3) Absorption spectra of 5-cm crystals of ultrapure benzene indicate that the ${}^3E_{1u}\leftarrow{}^1A_{1g}$ transition lies higher than 36 900 cm^{-1} providing its oscillator strength is of the expected magnitude.

(4) That this absorption is the second triplet is evidenced by the following facts:

(a) *In the O_2-perturbed system, the second triplet and the first triplet were observed in all instances during the same experiment in the same sample, and with approximately constant relative intensities.*

(b) The relative intensities of the three absorptions (${}^1B_{2u}$, ${}^3B_{1u}$, ${}^3E_{1u}\leftarrow{}^1A_{1g}$) are roughly of the expected magnitude.

(c) The absorption is indeed O_2 enhanced. This meets a criterion for a multiplicity-forbidden transition.

(d) The position of the absorptions is reasonable.

CONCLUSIONS

In the past, the search for the second triplet of benzene has usually been carried out at room temperature and in the liquid phase,[26] using O_2- and heavy-atom-perturbation methods.[27] In all of these attempts no great pains were taken to purify the benzene or the perturbers. It is obvious from the earlier discussion that experiments of this nature are not likely to give positive evidence about higher triplet states in benzene. Hot bands, impurities, and spreading out of intensity are just a few of the reasons that data from such experi-

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[25] G. C. Nieman and G. W. Robinson, J. Chem. Phys. **39**, 1298 (1963); E. R. Bernstein, S. D. Colson, R. Kopelman, and G. W. Robinson (to be published).

[26] A. C. Pitts, J. Chem. Phys. **18**, 1416 (1950); J. S. Ham and K. Ruedenberg, *ibid.* **25**, 1 (1956).

[27] For a general review of these experiments see Ref. 1.

ments are not definitive. Bands observed by Ham[28] at 77°K in a carbon tetrachloride glass have been assigned[29,30] as the (0, 0) progression of the $^1B_{2u}\leftarrow{}^1A_{1g}$ transition intensified by solvent–solute interactions. We consider this assignment to be much more reasonable than the original suggestion that the Ham bands are the second triplet.

Even though positive identification of the broad absorptions observed in our 5-cm samples of pure benzene, as belonging to the $^3E_{1u}\leftarrow{}^1A_{1g}$ transition, is not possible, these experiments are very useful in placing a lower limit to the energy of this state. The $^3E_{1u}$ state of crystalline C_6H_6 cannot lie below 36 900 cm^{-1}. In the O_2-perturbed C_6H_6 system no absorption (aside from the first triplet) was observed below 36 560 cm^{-1}. These results are consistent with the empirical lower limit of 37 000–38 000 cm^{-1} for the $^3E_{1u}\leftarrow{}^1A_{1g}$ transition as discussed by Platt.[1]

Pariser–Parr theory[4] places the position of maximum intensity of the $^3E_{1u}\leftarrow{}^1A_{1g}$ transition exactly halfway between the maxima of the $^3B_{1u}\leftarrow{}^1A_{1g}$ and the $^1B_{2u}\leftarrow{}^1A_{1g}$ transitions. Due to the lack of experimental data, these authors were forced to employ empirically evaluated integrals derived from the energies of observed singlet states to calculate triplet-state energies. There is no theoretical justification for this, since singlet and triplet wavefunctions, even though from a common configuration, are expected to require a different basis representation. The discrepancy between our experimental energy and that calculated for the $^3E_{1u}$ state on the basis of Pariser–Parr theory is about 3000 cm^{-1}. This value is based on (0, 0) band positions (see Table I) rather than on absorption maxima as specified in the theory, but for the states in question there should be no great difference.[31] Thus, the second triplet lies nearly $\frac{9}{10}$ rather than $\frac{1}{2}$ of the way from the lowest triplet to the lowest excited singlet state of benzene.

It should be noted that from our experiments no information can be obtained concerning the energy of the proposed O_2–benzene charge-transfer states.[29] These states would have a continuous absorption spectrum and therefore could not be differentiated from light loss due to scattering in the deposit experiments.

Note added in proof: It is conceivable that the absorption observed in the 37 000-cm^{-1} region of the O_2-perturbed system is due to the benzene–O_2 "double" transition $[^3B_{1u}\,{}^1\Delta_g]\leftarrow[^1A_{1g}\,{}^3\Sigma_g^-]$. Addition of the gas-phase value of the $^1\Delta_g\leftarrow{}^3\Sigma_g^-$ transition to the crystal-phase value of the $^3B_{1u}\leftarrow{}^1A_{1g}$ transition "predicts" the double transition to lie about 1000 cm^{-1} above that observed. This is not particularly close. Nevertheless, it would be unrealistic to exclude this as a possibility, considering the assumptions inherent in the prediction. Observing the transition using NO perturbation would eliminate this possibility. Deposit experiments were attempted in which the O_2 was replaced by NO. These proved to be unproductive as NO is a weaker perturber than O_2, neither the first nor second triplet being observed. We are now working on new techniques that will hopefully yield long, transparent crystals of benzene containing NO. NO–benzene mixed crystals about 2 cm long have been produced, but so far have been so badly cracked that they are opaque in the 37 000-cm^{-1} region. The first triplet has, however, been detected in such crystals. We are also trying to grow crystals long enough to observe the first triplet ($^3B_{1u}\leftarrow{}^1A_{1g}$) transition in the absence of external perturbations. We acknowledge B. Stevens of Sheffield University for suggesting the double transition to Robinson as a possible cause of the 37 000-cm^{-1} absorptions in the benzene–O_2 mixed crystal. It should not be forgotten, however, that similar absorptions have been seen in 5-cm crystals containing no O_2 where, of course, the double transition cannot occur.

ACKNOWLEDGMENTS

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[28] J. S. Ham, J. Chem. Phys. **21**, 756 (1953).

[29] E. C. Lim and V. L. Kowalski, J. Chem. Phys. **36**, 1729 (1962).

[30] N. S. Bayliss and L. Hulme, Australian J. Chem. **6**, 257 (1953).

[31] A recent theoretical calculation (Ref. 5) which employs more extensive configuration interaction within the framework of the Pariser–Parr theory, appears to give very good agreement with our experimental $^3E_{1u}$ energy. However, the calculated energies refer to intensity maxima. The theoretical (0–0) band position is 1000 to 2000 cm^{-1} lower than our experimental value. It should also be noted that "experimental values" for the $^3E_{1u}$ energy reported in Refs. 3 and 5 are not experimental values at all, only semiempirical estimates.