

Singlet triplet absorption spectra of charge transfer complexes of naphthalene
by Raymond Graham

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemistry
Montana State University
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Abstract:
The singlet-triplet spectra of charge-transfer complexes with arsenic trichloride, antimony trichloride, bismuth trichloride, mercuric acetate, mercuric chloride, and mercuric bromide were examined. The intensities of these enhanced singlet-triplet bands were found to depend on spin-orbit coupling in the metal ion of the inorganic salt and the strength of the charge-transfer complex. The order of effectiveness of these salts as heavy-atom perturbers was found to be: bismuth trichloride > mercuric bromide > mercuric chloride > antimony trichloride > mercuric acetate > arsenic trichloride.

The singlet-triplet spectra of phenylmercurie acetate, diphenyImercury, and the mercuric chloride-benzene complex were also studied. The heavy-atom effect was found to be greater in the covalently bonded mercury compounds.

SINGLET TRIPLET ABSORPTION SPECTRA OF CHARGE TRANSFER COMPLEXES OF NAPHTHALENE

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of

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ABSTRACT

The singlet-triplet spectra of charge-transfer complexes with arsenic trichloride, antimony trichloride, bismuth trichloride, mercuric acetate, mercuric chloride, and mercuric bromide were examined. The intensities of these enhanced singlet-triplet bands were found to depend on spin-orbit coupling in the metal ion of the inorganic salt and the strength of the charge-transfer complex. The order of effectiveness of these salts as heavy-atom perturbers was found to be: bismuth trichloride > mercuric bromide > mercuric chloride > antimony trichloride > mercuric acetate > arsenic trichloride.

The singlet-triplet spectra of phenylmercuric acetate, diphenylmercury, and the mercuric chloride-benzene complex were also studied. The heavy-atom effect was found to be greater in the covalently bonded mercury compounds.

INTRODUCTION

I. NATURE OF PROBLEM

There are many conflicting arguments proposed concerning the location and assignment of triplet energy levels in aromatic compounds. The principal methods of examining these triplet states are either by phosphorescence or singlet-triplet absorption measurements. Since singlet-triplet transitions are highly forbidden (oscillator strengths of less than ca. 10^{-5}), either long pathlengths or intensity enhancement techniques must be used for spectral absorption. In long pathlengths of aromatic compounds impurity absorptions and hot band structure from nearby intense singlet-singlet transitions become dominant. Hot bands are vibrationally allowed transitions from thermally populated higher vibrational states.

Singlet-triplet enhancement techniques are classified as either heavy-atom or paramagnetic perturbations. Two different mechanisms are proposed for these enhancements. One is an exchange mechanism and the other is of a charge-transfer nature. It is not clear if one of these mechanisms will have greater importance than the other. In either case, spin-orbit coupling seems to be the major factor affecting these enhancements. The nature of this coupling, for a many electron system, is not fully established, and a precise spin-orbit interaction operator is not known.

Since there is some doubt about the nature of singlet-triplet intensity

enhancements, it was decided to examine the effect of certain heavy atoms (either in molecules or in the atomic state) on the intensity of these transitions in certain aromatic hydrocarbons. This research originally consisted of examining the effect of atomic mercury on the singlet-triplet transitions of benzene at low temperatures. For various reasons, to be discussed later, no singlet-triplet transitions were observed by this method. Since naphthalene and benzene form charge-transfer complexes with some salts of Group 2b, 4a, and 5a elements, the effects of these salts on the singlet-triplet transitions of benzene and naphthalene were studied. Also the spectra of diphenyl mercury and phenylmercuric acetate were examined in order to compare the enhancement effects of a covalently bonded heavy atom to one that was weakly bonded (mercuric chloride-benzene complex).

II. SINGLET-TRIPLET TRANSITIONS

The intensity of a spectral line is proportional to the transition moment integral M_{lk} (4, 38),

$$M_{lk} = \left\langle \psi_{\ell} | \hat{o} | \psi_{k} \right\rangle ,$$

where ψ_{ℓ} and ψ_{k} are the wave functions for the final and initial states, respectively, and $\hat{o}$ is the operator representing the mechanism (electric or magnetic dipole or quadrupole, for instance) responsible for the change of state of the molecule. Selection rules are predictions concerning the value of this integral. These selection rules determine the conditions for which this transition moment integral will have either zero or nonzero values. One of the well-known selection rules of atomic and molecular spectroscopy is $\Delta S = 0$; that is, only transitions between states with the same multiplicity are allowed. This selection rule, called the "prohibition of intercombinations", only applies for Russell-Saunders coupling, where S is a well defined quantum number.

The selection rule, $\Delta S = 0$, may be derived in the following manner. If spin-orbit coupling is ignored, the wave function for an electronic state may be written as a product of an orbital and a spin function

$$\psi_{es} = \psi_{e\beta}$$

where ψ_{e} is the orbital part and β is the spin part of the wave function. The transition moment integral for a transition between states 1 and k may be written as

$$M_{\ell k} = \langle \psi_{es,\ell} | \vec{M} | \psi_{es,k} \rangle = \langle \psi_{e,\ell} | \vec{M} | \psi_{e,k} \rangle \langle \beta_{\ell} | \beta_{k} \rangle$$

where $\vec{M}$ is the dipole moment vector. Since the spin functions are orthogonal, the second integral on the right vanishes for states with different spin. Thus transitions between states with different multiplicities are forbidden. This section rule only applies if spin-orbit coupling is ignored. When spin-orbit coupling is considered, the wave function may no longer be written as a simple product of an orbital and a spin function. This means that the above equation no longer holds and the transition moment ($M_{\ell k}$) may be non-zero for spin forbidden transitions.

In atomic spectroscopy, there are two coupling schemes used to explain the interaction of orbital angular momentum with spin angular momentum. Russell-Saunders coupling applies for light atoms, while the second scheme, (j, j) coupling, applies for the heavier atoms. The Russell-Saunders scheme assumes that the interaction between l_i (orbital angular momentum) and s_i (spin angular momentum) are so strong between the individual l_i terms and between the various s_i terms that they combine to give resultant L and S (Σl_i = L and Σs_i = S). The L and S then combine to give the resultant J (total angular momentum). This coupling scheme holds fairly well for second row atoms (spin-orbit coupling energy is very small) but the validity of the Russell-Saunders coupling scheme deteriorates rapidly with increasing atomic number.

The (j, j) coupling scheme assumes that there is considerable interaction

between each individual l_i and s_i. These combine to give a resultant j_i. The j_i then combine to give the total angular momentum (J) of the atom. Pure (j, j) coupling seldom occurs and most atoms are intermediate cases of these two coupling schemes.

It can be seen from the above discussion that L and S are "good" quantum numbers only when the Russell-Saunders coupling scheme is valid. For light elements, the validity of these quantum numbers is not seriously impaired. On the other hand, for the elements of rows V and VI of the periodic table (for elements like cadmium, tin, antimony, mercury, lead, and bismuth), L and S are not good quantum numbers. In these elements, the spin-orbit coupling energy is quite large. This has the effect of scrambling together states of different multiplicities. Because of this, "spin forbidden" transitions become allowed in these heavy atoms.

III. THE EFFECT OF SPIN-ORBIT COUPLING ON SINGLET-TRIPLET TRANSITIONS

The derivation of the selection rule, $\Delta S = 0$, contains a major approximation concerning the wave functions used in the evaluation of the transition moment (38). These wave functions are eigenfunctions of the one-electron Hamiltonian h_j,

$$h_j = (h^2/2m)\nabla_j^2 - Ze^2/r_j$$

The Hamiltonian h_j is not complete and in the absence of external fields should contain terms that are due to electron spin. In one electron spectra, the effect of spin arises from an interaction between the magnetic moment of the spinning electron and the magnetic field due to its orbital motion about the nucleus (spin-orbit interaction).

For molecules where relativistic effects are small, the part of the Hamiltonian that depends on electron spins may be written as the sum of two interactions, H' and H'' (38). H' and H'' are the spin-orbit and the spin-spin parts of the Hamiltonian, respectively. The corrected Hamiltonian now becomes

$$H = H_0 + H' + H''$$

Since H' and H'' are much smaller than H_0, the wave functions of H may be obtained from the eigenfunctions of H_0 by means of perturbation theory.

The nature of the spin-orbit part of the Hamiltonian operator may be obtained from classical spin-orbit theory. The magnetic moment of a spinning

electron is related to its angular momentum by (9)

$$\vec{\mu} = -(|e|/mc)\vec{s}$$

The interaction energy between this magnetic dipole moment and the magnetic field due to the orbital motion of an electron with velocity $\vec{v}$ and in the electric field (E) of the nucleus is classically given by

$$H' = -\vec{\mu} \cdot (\vec{E} \times \vec{v})$$

$$\text{or } H' = +(|e|/2mc^2)(\vec{E} \times \vec{v}) \cdot \vec{s}$$

where the factor 1/2 is included for relativistic purposes. Since the momentum $\vec{p}$ is equal to $m\vec{v}$ and $\vec{E}$ is the gradient of the scaler potential V of the electron in the nuclear field, the spin-orbit Hamiltonian may be written as

$$H' = (\overrightarrow{\text{grad}v} \times \vec{p})/(2m^2c^2)$$

For a general many electron potential field $V = V(r_i)$, this spin-orbit Hamiltonian becomes

$$H' = (1/2m^2c^2)\sum_i (1/r_i)(\partial V(r_i)\vec{L}_i\vec{S}_i = \sum_i \xi(r_i)\vec{L}_i\vec{S}_i$$

where the sum is over all the electrons.

The above derivation does not give the complete spin-orbit Hamiltonian. The total spin-orbit Hamiltonian is given by (56)

$$\mathcal{H}_{SO} = \alpha^2 \sum_{\mu i} \frac{Z\mu \vec{L}_i \cdot \vec{S}_i}{r_i^3 \mu} - \sum_{i,j} \frac{\vec{P}_i \times \vec{r}_{ij}}{r_i^3{}_j} \cdot \vec{S}_i + 2\sum_{i,j} \frac{\vec{P}_j \times \vec{r}_{ij}}{r_i^3{}_j} \cdot \vec{S}_i$$

where α is the fine structure constant ($\alpha = e^2/hc$), P is the linear momentum operator, $Z\mu$ is the effective nuclear charge of the μth nucleus. This first term in the bracket is the previously derived partial spin-orbit Hamiltonian and

represents the coupling of the spin and the orbital momentum of an electron in the presence of an attractive nuclear field Z_μ. The coupling of the spin and the orbital motions of electron i with the repulsive field of electron j is represented by the second term. The third term represents the interaction between the spin of one electron and the spin of another electron and is usually very small. The importance of the second term decreases with increasing nuclear charge. Here, it will be assumed that the partial spin-orbit Hamiltonian (H') is the controlling factor in the spin-orbit interaction and the other terms in the spin-orbit Hamiltonian will be ignored.

For an atomic system, the effect of spin-orbit coupling may be investigated with first-order perturbation theory. The approximate spin-orbit coupling energy may be obtained by evaluating the matrix elements of H' with the eigenfunctions of H_0 (the Hamiltonian without spin-orbit interaction) (9, 70). The one-electron eigenfunctions of H_0 may be written in terms of the quantum numbers n, m_l, and m_s;

$$\varphi(n, l, m_l, m_s) = R(n, l)\, F(l, m_l, m_s)$$

where $R(n, l)$ and $F(l, m_l, m_s)$ are the radial and angular parts of the one-electron eigenfunction, respectively. The matrix elements of H' may then be written as

$$\left\langle \varphi(n, l, m_l, m_s) \left| \xi(r) L.S \right| \varphi(n', l', m'_l, m'_s) \right\rangle$$

$$= \left\langle R(n, l) \left| \xi(r) \right| R(n', l') \right\rangle \left\langle F(l, m_l, m_s) \left| L.S \right| F(l', m'_l, m'_s) \right\rangle$$

The L. S matrix is equal to zero unless $l = l'$ and $m_l + m_s = m'_l + m'_s$. In the case of a Coulomb potential, $V(r) = -Ze^2/r$, the matrix element $\zeta(r)$ may be evaluated in terms of the spin-orbit coupling constant

$$\zeta_{nl} = \frac{4\pi^2}{h^2}\zeta_{nl} = \frac{e^2Z^4}{2m^2c^2a^3n^3l(l+1)(l+\frac{1}{2})}$$

The relative importance of spin-orbit coupling in an atom is given by the magnitude of the spin-orbit coupling constant. The important point to notice here is the strong dependence of ζ_{nl} on the atomic number (Z) (heavy-atom effect).

The effect of spin-orbit interaction of the wave functions of a polyatomic molecule is to mix functions which have different multiplicities (29, 56). Thus the singlet states of a molecule may have a small amount of triplet character and the triplet states a small amount of singlet character. According to the first order perturbation theory, the singlet ground state wave function for a polyatomic molecule may be written as

$$^1\psi_o = {}^1\psi_o^o + \sum_j \delta_{oj}\, {}^3\psi_j^o$$

where

$$\delta_{oj} = \frac{\langle {}^1\psi_o^o | H' | {}^3\psi_j^o \rangle}{|{}^1E_o - {}^3E_j|}$$

Here the summation is carried out over the triplet manifold, and δ_{oj} is the mixing coefficient between $^1\psi_o^o$ and $^3\psi_j^o$. Similarly, the lowest triplet state wave function is given by

$$^3\psi_1 = {}^3\psi_1^o + \sum_k \delta_{1k}\, {}^1\psi_k^o$$

where the summation is carried out over all the states in the singlet manifold.

The probability of a radiative transition between $^1\psi_o$ and $^3\psi_1$ is proportional to the square of the transition moment $M(S_o, T_1)$.

$$M(S_o, T_1) = \langle {}^1\psi_o | \vec{M} | {}^3\psi_1 \rangle = \langle {}^1\psi_o{}^o | \vec{M} | {}^3\psi_1{}^o \rangle + \langle \Sigma\delta_{oj}\, {}^3\psi_j{}^o | \vec{M} | \Sigma\delta_{1k}\, {}^1\psi_k{}^o \rangle$$
$$+ \langle {}^1\psi_o{}^o | \vec{M} | \Sigma\delta_{1k}\, {}^1\psi_k{}^o \rangle + \langle \Sigma\delta_{oj}\, {}^3\psi_j{}^o | \vec{M} | {}^3\psi_1{}^o \rangle$$
$$+ \langle \delta_{1o}\, {}^1\psi_o | \vec{M} | {}^1\psi_o{}^o \rangle + \langle \delta_{o1}\, {}^3\psi_1{}^o | \vec{M} | {}^3\psi_1{}^o \rangle$$

where $\vec{M}$ is the dipole moment operator. The first and second terms in the expanded expression vanish because of spin orthogonality. The transition moment now becomes

$$M(S_o, T_1) = \Sigma\delta_{1k} M(S_{o1} S_k) + \Sigma\delta_{oj} M(T_{11} T_2) + \delta_{1o} M(S_{01} S_o) + \delta_{o1} M(T_{11} T_1)$$

The last two terms in this expression depend on the ground state and the excited state dipole moments and vanish for nonpolar molecules (naphthalene and benzene). Thus for nonpolar molecules there are two sources of intensity for singlet-triplet transitions. The first source of intensity is characteristized by a spin-orbit interaction between the first excited triplet state and those excited singlet states to which transitions from the ground state are allowed. The intensity is "stolen" from allowed singlet-singlet transitions with transition moment $M(S_o, S_k)$. The second source of intensity is the process in which there is a spin-orbit interaction between the ground state and those excited triplets in which transitions from the lowest triplet are allowed. This

process steals intensity from the triplet-triplet transitions with transitions moments $M(T_l, T_k)$.

These two sources of intensity for singlet-triplet transitions depend on two factors: the intensities of near-by singlet-singlet and triplet-triplet transitions and the amount of spin-orbit coupling present in the molecule. Since this spin-orbit interaction increases with atomic number, the presence of a heavy atom, either internal or external, should increase the probability of a singlet-triplet transition in a polyatomic molecule. This gives rise to the heavy-atom effect.

IV. ASSIGNMENT OF TRIPLET ENERGY LEVELS IN AROMATIC COMPOUNDS

Even with spin-orbit interaction considered, the transition probabilities of singlet-triplet transitions in most aromatic compounds are generally small. Because of this, the identification of triplet states for most aromatic compounds has been difficult. Kearns (52) reviewed this problem for catacondensed aromatic hydrocarbons, and Platt (76) gives a critical review of the particular problem of locating the second triplet of benzene. Both Platt and Kearns list the possible criteria for determining the assignments of triplets states of aromatic compounds. They divide these criteria into two categories: weak and strong. Weak criteria include agreement of the position and intensity of the observed band with the calculated location and intensity. Strong criteria include the McClure (57-59) enhancement of singlet-triplets by heavy-atom or paramagnetic substituents and Kasha enhancement (50) of singlet-triplet transitions by heavy-atom or paramagnetic solvent molecules.

Platt (76) has reviewed the evidence for the assignment of the lowest two triplet states of benzene. He concludes that there is little doubt in the assignment of the lowest as $^3B_{lu}$ (although Hochstrasser (42) has recently indicated a possible ambiguity). Although there is some doubt about the assignment of the second triplet, Platt indicates that it is very probably the $^3E_{lu}$ state. Experimentally the $^3B_{lu}$ state has been identified with observed bands at ca. 31kK. Platt points out that the proof is unanimous for this assignment. The location

of the second triplet has been more difficult. Theoretically the second triplet is predicted to lie between 33 and 40 kK (1, 36, 52, 72, 76). Recently, Colson and Bernstein (8) have observed some bands at ca. 36.6 kK (both in thick single crystals of pure benzene and in paramagnetically enhanced thin films). These bands have been tentatively assigned to the $^3E_{1u} - {}^1A_{1g}$ transition.

The lowest triplet of naphthalene is predicted to be a $^3B_{2u}$ species (49, 62). This triplet state has been identified with the observed bands at ca. 21.3 kK. Experimentally, these bands have been studied by several methods. Kasha (50) first observed these bands using a heavy-atom enhancement technique, and Evans (24) used a paramagnetic enhancement technique to locate them. Hanson and Robinson (40) have measured the positions of these singlet-triplet bands in crystalline naphthalene. In 1966, Marchetti and Kearns (65) used the phosphorescence excitation method to observe these bands.

V. HEAVY-ATOM ENHANCEMENT TECHNIQUES

Kasha (50) first noticed that when the colorless pure liquids, α-chloronaphthalene and ethyl iodide were mixed, a yellow color was produced even though no chemical reaction occurred. The explanation was that the lowest singlet-triplet absorption band of the naphthalene molecule was greatly enhanced in intensity in the presence of ethyl iodide. That is, according to the previous discussion, the proximity of the heavy atom (iodine) in the solvent perturbs the Russell-Saunders coupling valid in low Z electronic systems. This causes a relaxation of spin quantization and increases the singlet-triplet transition probability.

McGlynn, Azumi, and Kasha (61) examined the effects of a variety of solvents on the intensities of the lowest singlet-triplet transition of several organic molecules. Some of the solvents used contained atoms of large atomic number (heavy atoms). It was shown that these heavy-atom solvents increased the singlet-triplet absorptivity, and that this enhancement was unique for singlet-triplet transitions (that is, no enhancement of singlet-singlet bands occurred). They also verified that this perturbation was of a spin-orbit nature (by varying the spin-orbit nature of the heavy-atom solvent).

Studies have been reported on the heavy-atom enhancement of singlet-triplet transitions in benzene, both as intramolecular substitution (57) and as intermolecular solvent effects (8, 19, 59, 60, 61, 62, 77, 81). Robinson (77) has studied the lowest singlet-triplet transition of benzene in crystalline rare

gas solvents. He found that the order of effectiveness of the rare gases as heavy-atom perturbers was : Xe>Kr>Ar>Ne. This order agrees with the supposition that nuclear charge is the limiting parameter for effecting mixing of singlet and triplet states.

Murrell (70, 71) and Hoijtink (44) have shown that there are two mechanisms whereby the singlet-triplet transitions can become allowed through the influence of a heavy atom. The first mechanism involves the mixing of excited singlet and excited triplet states of the organic molecule. Excited states of the heavy-atom perturber are mixed with excited singlet states of the organic molecule (mixing involves two-electron exchange integrals between the orbitals of the hydrocarbon and those of the heavy-atom perturber) which are in turn mixed with the triplet state. The second mechanism involves mixing in which both the singlet and triplet states of hydrocarbon mix with a charge-transfer state. Murrell (70, 71) has shown that both mechanisms predict that the intensity of the singlet-triplet transition will be proportional to the fourth power of the overlap integral between orbitals of the perturber and the perturbed molecule. Considering this, one cannot rule out one mechanism in favor of the other. Nevertheless, Murrell (70, 71) and Tsubomura and Mulliken (80) have indicated that the charge-transfer mechanism is likely to be more important for the benzenoid hydrocarbons.

VI. CHARGE-TRANSFER COMPLEXES

The term charge-transfer complex is used to describe certain types of weakly bonded complexes. These complexes are formed by weak interactions between two substances one of which acts as electron donors and the other as an electron acceptor. Many donor-acceptor complexes are unstable and only exist in equilibrium in solutions. The rates of formation of these complexes are very rapid and generally kinetics studies cannot be made by ordinary procedures. The heats of interaction are generally small and the degree of electron transfer to the acceptor molecule is much less than when ordinary covalent compounds are formed.

Donor molecules can be either inorganic or organic in nature, however complexes with organic molecules only are of interest here. Organic substances that can serve as electron donors can be classified into two groups (2). The first group consists of compounds having non-bonding (lone pair) electrons available for coordination (n-donors). This group includes alcohols, organic sulfides and iodides, and nitrogen bases. The second group, which is of interest here, consists of compounds having pi-electrons available for sharing (pi-donors). Examples of this type are alkenes, alkynes, and aromatic hydrocarbons and their substitution products.

Acceptor molecules include a wide range of chemical compounds. These include organic hydroxylic compounds, organic pi-acids, Friedel-Crafts catalysts, and others. Hydroxylic compounds form hydrogen bonded complexes with

many n-donors. These can be loosely classified as charge-transfer complexes. One of the strongest pi-acids is tetracyanoethylene. This substance forms brillantly colored solutions in aromatic hydrocarbons and other donor solvents (2).

Friedel-Crafts catalysts are Lewis acids and therefore readily accept electrons from many donor compounds. The most common Friedel-Crafts catalyst, aluminum trichloride, forms complexes with both n and pi-donors (2). Aluminum tribromide forms a faintly yellow colored complex with benzene (7). The molecular formula for this complex was reported as $C_6H_6 \cdot Al_2Br_6$.

The inorganic salts of the elements of Groups 2b, 4a, and 5a (only the salts of zinc, cadmium, mercury, tin, lead, arsenic, antimony, and bismuth are of interest here) can be classified, to varing degrees, as Lewis acids and therefore act as electron acceptors. Charge-transfer complexes of salts of a few of these elements with both n and pi-donors have been reported. Here, the interest lies in complexes of salts of these elements with aromatic hydrocarbons (mainly naphthalene and benzene).

Molecular complexes of naphthalene and benzene with a few of these Lewis acids have been known for quite some time. In 1882, Smith and Davis (79) reported that antimony trichloride formed crystalline molecular addition compounds with naphthalene and benzene. They reported the molecular formulas of these compounds as $3SbCl_3 \cdot 2C_{10}H_8$ and $3SbCl_3 \cdot 4C_6H_6$. These formulas now

seem to be incorrect. Around the turn of the century, Menshutkin (66) studied systems of antimony tribromide and trichloride with several organic compounds (now known as Menshutkin complexes). Menshutkin examined the phase diagrams of these systems and found that systems of both antimony trichloride and antimony tribromide with naphthalene formed compounds with congruent melting points (stable complexes were formed). These compounds had compositions of $2SbCl_3 \cdot C_{10}H_8$ (melting point 86°C) and $2SbBr_3 \cdot C_{10}H_8$ (melting point 66°C).

The electronic absorption spectrum and dipole moment of a one to one molecular complex between stannic chloride and naphthalene have been reported (82). A strong absorption in the near ultraviolet was interpreted as being caused by a charge-transfer transition. Kawalec (51) reported that both 1- and 2-methylnaphthalene and antimony trichloride formed stable compounds with the composition $2SbCl_3 \cdot CH_3C_{10}H_7$. Pure crystals of these compounds were pale yellow in color. Much work has been done on the nuclear quadrupole resonance (NQR) spectra of the complexes of naphthalene with antimony trichloride and tribromide (30-36). Grechishkin and Kyuntsel (30) concluded from NQR spectra that the antimony atom in the antimony tribromide-naphthalene complex is, to a large degree, the acceptor. They also found that there are three nonequivalent bromide atoms in the lattice of this complex.

The infrared and Raman spectra of the antimony trichloride-benzene complex have been investigated (11, 27, 28). The infrared spectrum was

interpreted as showing a decrease in symmetry from D_{6h} for pure benzene to C_{6V} for the complex. This interpretation seems to be incorrect, and Daasch (11) has reported that the symmetry of the complex is most probably C_{3V} (in a staggered form).

Hulme and Szymanski (48), from X-ray crystallography data, recently reported the crystal structure of the 2:1 complex of antimony trichloride and naphthalene. The structure consisted of antimony trichloride molecules stacked in the bc plane alternating with layers of naphthalene molecules in the plane x = 1/2. The antimony atoms existed in a 4-coordinated, distorted sp^3d trigonal bipyramidal environment, with two chlorine atoms in equatorial positions and the third chlorine atom occupying an axial position. The third equatorial position was filled by the antimony lone pair, and the other axial position was used in the bonding to the pi-system of the naphthalene molecule. The distance from the antimony atom to the plane of the naphthalene molecule was 3.2 A. The naphthalene bond distances and angles were distorted from those of crystalline naphthalene (see figure 1).

Charge-transfer complexes have been described using molecular orbital theory in two related but slightly different ways. These descriptions are due to Mulliken (68) and Dewar (12, 13, 14). Mulliken represents a charge-transfer complex as a resonance hybrid of a "no bond" type structure and an ionic structure. The ground state wave function for such a complex is given by

$$\psi_N = a\psi(A, B) + b\psi(A^+B^-), \text{ where } a \gg b.$$

$\psi(A, B)$ is the wave function for the "no bond" structure, and $\psi(A^+B^-)$ is the wave function for the ionic structure. The acceptor A and donor B may in general be any two suitable species in which the ionization potential of A is greater than that of B. The excited state wave function is given by

$$\psi_E = -b\psi(A, B) + a\psi(A^+B^-), \text{ where } a \gg b$$

The "no bond" wave function, $\psi(A, B)$, has the form

$$\psi(A, B) = \mathcal{A}\psi_A\psi_B + \ldots$$

Here $\mathcal{A}$ denotes that the product $\psi_A\psi_B$ of the wave functions of A and B are to be made antisymmetric with respect to all electrons. The wave function $\psi(A^+B^-)$ represents a transfer of an electron from A to B accompanied by the formation of an ionic bond.

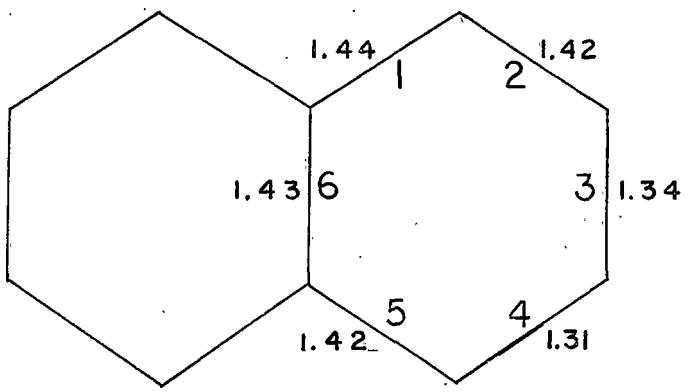


Figure 1. Naphthalene bond distances for the antimony trichloride-naphthalene complex (from the structural data of Hulme and Szymanski (48)).

Using Mulliken's scheme, the energies of the ground state and the first excited state of a charge-transfer complex may be approximated using second order perturbation theory (67). The ground state energy is given by

$$W_N = W_O - (H_{O1} - W_O S)^2 / (W_1 - W_O)$$

and the excited state energy by

$$W_E = W_1 + (H_{O1} - W_1 S)^2 (W_1 - W_O)$$

where

$$W_O = \langle \psi(A, B) | \mathcal{H} | \psi(A, B) \rangle$$

$$W_1 = \langle \psi(A^+B^-) | \mathcal{H} | \psi(A^+B^-) \rangle$$

$$H_{O1} = \langle \psi(A, B) | \mathcal{H} | \psi(A^+B^-) \rangle$$

$\mathcal{H}$ is the complete Hamiltonian for the complex, and $W_O - W_N$ is the ground state resonance energy and usually ranges from 0 to 10 Kcal/mole for this type of complex.

Charge-transfer complexes are characterized by the appearance of a new electronic absorption band which does not appear in the spectra of the acceptor or donor alone. According to Mulliken's theory this new band is attributed to a transition from the ground state (ψ_H) which has very little ionic character to an excited state (ψ_E) which is mostly ionic. The energy of this transition is equal to difference in energy of the ground state and the excited

state. These complexes may also have other excited states which correspond to excitation of the acceptor or donor alone. The absorption bands caused by excitation to these excited states will not differ very much from the bands of the separate molecules.

Dewar (12, 13, 14, 15) used molecular orbital theory to describe the charge-transfer complex A, B in terms of interactions between the orbitals of A and B. These interactions may be characterized by considering the orbital diagram in figure 2.

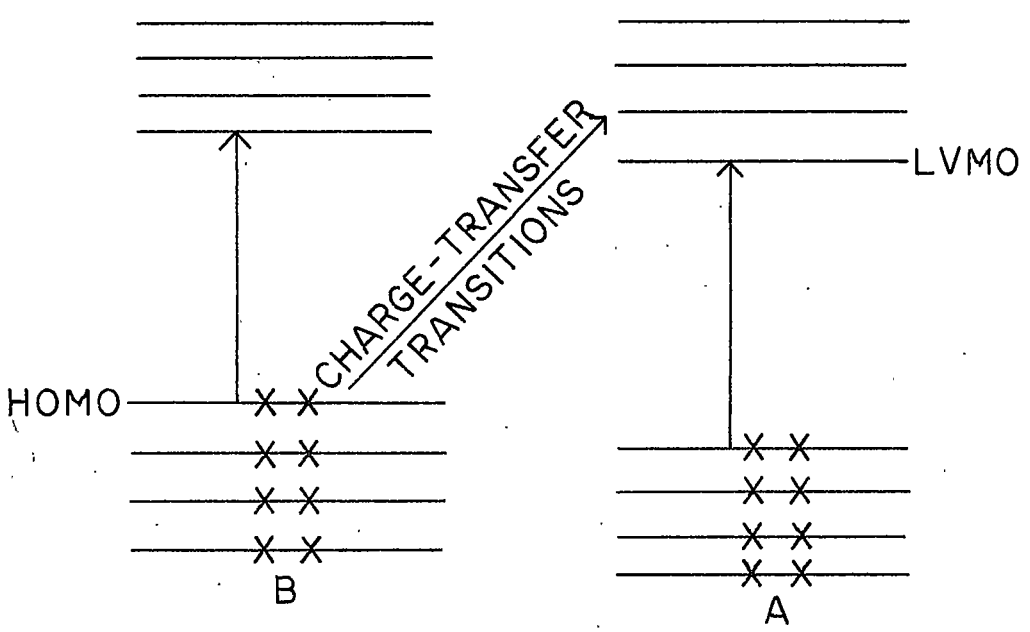


Figure 2. Schematic representation of the electronic transitions in a charge-transfer complex. HOMO equals highest occupied molecular orbital and LVMO equals lowest vacant molecular orbital.

Interactions of the filled bonding orbitals of A and B will not lead to any change in their total energy and to no net transfer of charge between A and B. Interaction of the filled orbitals of A (or B) with the empty antibonding orbitals of B (or A) depress the former and raise the latter with a simultaneous transfer of charge from A (or B) to B (or A). These interactions are inversely proportional to the difference in energy between the interacting orbitals. Since the donor has filled orbitals of relatively high energy and the acceptor had empty orbitals of relatively low energy, the main interaction is between the filled orbitals of the donor and the empty orbitals of the acceptor. This will give a net transfer of charge from the donor B to the acceptor A.

Dewar explains the appearance of a new band in the electronic spectrum of the complex as a transition between the highest occupied molecular orbital (HOMO) of the donor (B) to the lowest vacant molecular orbital (LVMO) of the acceptor (A). The locally excited transitions of the donor and the acceptor should not differ much from the transitions of the separate molecules.

Using this scheme, the energy of a charge-transfer complex (for pi-pi complexes) may be written in terms of energies of the orbitals of the acceptor and the donor (14). This energy is given by

$$E_{CT} = A_j - D_i = A_j - \alpha - \beta X_i$$

α is the coulomb energy of carbon, β is the carbon-carbon resonance energy and X_i is a quantity calculated theoretically which relates to the energy of the highest

filled orbital of the donor.

The energy of a charge-transfer transition may be related to the donor ionization potential (I_D) and the electron affinity of the acceptor (E_A). Qualitative evidence on the dependence of this transition energy on the ionization potential of the donor may be obtained by considering the positions of charge-transfer bands of certain aromatic complexes with iodine (2). Considering the following iodine complexes, benzene (λ_{max} = 2900A), toluene (λ_{max} = 3000A), and mesitylene (λ_{max} = 3300A), one can see that the energies of the charge-transfer transitions increase with increasing ionization potential of the donor. The quantitative relationship $h\nu_{CT} = I_D - E_A - W$ was obtained by considering the plot of I_D versus $h\nu_{CT}$ for 18 iodine complexes (W is a coulombic term) (6). Since this plot is linear, it was concluded that W for these iodine complexes is independent of the nature of the donor. Since electron affinities are not known for most compounds, no quantitative relationship between E_A and the energy of a charge-transfer transition can be obtained.

EXPERIMENTAL

I. LOW TEMPERATURE STUDIES

The purpose of these studies was to test atomic mercury as a heavy-atom perturber of the singlet-triplet transitions of benzene and related aromatic compounds. The method that was used modified the procedure of Robinson (77). This method consisted of depositing mercury and an aromatic compound simultaneously on a cold quartz plate and taking the spectrum of this film through quartz windows. A special stainless steel low temperature dewar and a vacuum manifold were constructed for this purpose (figure 3).

The following procedure was used for the plating out of mercury and aromatic compound. The system (figure 3) was evacuated and flushed with nitrogen. The dewar was filled with liquid air and the temperature allowed to come to equilibrium (ca. one hour). Mercury was located in the heated pyrex boat at C. A variac was connected to the nichrome wrapped glass boat in order to control the rate of deposition of mercury on the cold quartz plate. The aromatic compound (benzene in this case) was placed in a small flask at A, and the micrometer valve was opened slightly in order to get a slow rate of deposition of benzene. The rates of deposition of both mercury and benzene were varied in order to get thin films of good optical qualities. The deposition of mercury was also regulated so that the solid thin film contained ca. 5% mercury. Only very thin films could be obtained that had reasonable optical properties.

The ultraviolet spectrum of each film was then recorded.

A 1.5 meter Bausch & Lomb spectrograph was first used to record these spectra. A deuterium lamp was used as a light source, and the spectra were recorded on Kodak 103 ao photographic film. A variety of slit widths and exposure times were used for the recording of these spectra. No singlet-triplet transitions of benzene were observed in this manner. Following the same procedure as above, spectra of the thin films of mercury and benzene were also recorded using a 0.25 meter Bausch & Lomb monochromator (using the deuterium lamp as a light source). This monochromator was equipped with a P-28 photomultiplier and a D-C Amplifier and Electrometer (type 1230-A). These spectra were recorded on a Brown stripchart recorder (1 - 5 mv range). Again no singlet-triplet transitions were observed using this technique.

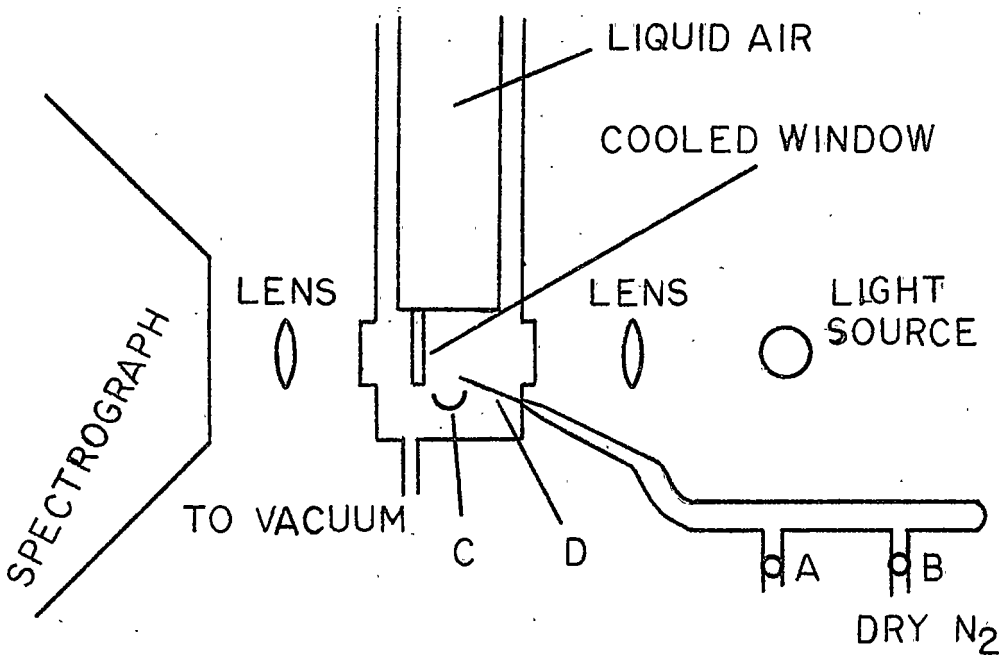


Figure 3. Schematic diagram of the apparatus used in the study of the effect of Hg on the spectra of aromatic hydrocarbons. Micrometer needle valves were located at A and B so that reproducible amounts of the aromatic hydrocarbon could be condensed on the cold surface. The heated pyrex boat at C was used for depositing the mercury onto the cold quartz surface. The capillary flow resistance (D) was used to keep a slight pressure differential between the manifold and the dewar. The aromatic compound was then sprayed through the nozzle (D) and condensed on the cold surface.

II. SPECTRA OF NAPHTHALENE AND NAPHTHALENE COMPLEXES

The singlet-triplet spectra of naphthalene and the naphthalene complexes were taken at 93 $\pm$ 2°C (liquid state spectra) on a Cary model 14 spectrometer. A tungsten lamp was used as the light source. These spectra were taken with either liquid naphthalene or air as a reference. In both cases either quartz or pyrex ground glass-stoppered cells (one, five, and ten centimeter cells) were used. When air was used as a reference the cell holder consisted of a metal tube wrapped with insulated material and resistance wire. This tube was placed in an insulated aluminum box designed to be used in a Cary 14 spectrometer. A variac was adjusted to hold the temperature at ca. 93°C.

The spectra with liquid naphthalene as a reference were taken in five centimeter glass-stoppered quartz cells coated with Instatherm (a commercial low resistance coating used for heating). The cell holders consisted of insulated aluminum boxes (equipped with pyrex windows) constructed to be used in the Cary 14 spectrometer. The temperature was controlled with a variac connected to a YSI Thermistemp Temperature Controller (model 71). The thermistor was located in the sample cell holder (in contact with the Instatherm coated cell) and the controller was adjusted to hold the temperature at 93 $\pm$ 2°C.

Baker and Adamsen resublimed naphthalene was used for all spectra without further purification. The purity of this naphthalene was checked using gas chromatography. These runs were made in the F & M (Model 400) gas

chromatograph at 175°C with helium as carrier gas and using flame ionization detection. The column was 16% Reoplex on Gas Chrom G, and redistilled hexane was used as a solvent. The gas chromagrams taken in this manner contained only one peak (other than the solvent peak) and indicated that the naphthalene was reasonably pure.

Reagent grade mercuric chloride, mercuric bromide, mercuric acetate, cadmium chloride, and lead chloride were used without further purification. Reagent grade antimony trichloride and bismuth trichloride were purified by sublimation under a vacuum at ca. 80 and 200°C, respectively. Reagent grade zinc chloride was purified by dissolving in concentrated hydrochloric acid and evaporating down to a paste. This paste was then dried under a vacuum at 120°C for approximately two weeks. Stannic chloride and arsenic trichloride were purified by vacuum distillation. The arsenic trichloride was distilled twice before using. The stannic chloride was distilled through a column packed with phosphorus pentoxide on glass wool (46).

Spectra were taken of both degassed and nondegassed solutions. The samples were degassed by bubbling commercial grade nitrogen through them for ca. one-half hour. The efficiency of degassing for this time period was checked by repetition of this process. After the first degassing no change was observed in the spectrum of pure naphthalene upon repeated degassings. The following spectra were taken in the above manner.

Naphthalene and Naphthalene Plus Oxygen

Naphthalene was saturated with oxygen and the singlet-triplet spectrum observed. This solution had a faint yellow color. The liquid naphthalene was then degassed and the singlet-triplet spectrum was taken again. These spectra were taken in 10 cm cells with air as a reference.

Naphthalene Plus Mercuric Chloride

Singlet-triplet spectra were taken of 0.05, 0.08, 0.09, 0.10, and 0.15 molal solutions of mercuric chloride in naphthalene. These spectra were taken of nondegassed solutions with air as a reference and using 10 cm cells. The singlet-triplet spectrum of a 0.15 molal solution was also taken with liquid naphthalene as reference and using 5 cm cells. Neither the sample nor the reference were degassed. The 0.10 solution was degassed four times with the singlet-triplet spectrum being taken after each degassing. Table I shows the results of these degassings.

The degassings in table I were carried out in the following manner. The samples were degassed (as discussed previously) and the spectra taken immediately except after the second degassing. There the sample was degassed and allowed to stand overnight before the spectrum was taken.

Naphthalene Plus Mercuric Bromide

The following singlet-triplet spectra were taken of the mercuric bromide

complex in 10 cm cells and with air as a reference: 0.05, 0.01, 0.15, and 0.20 molal solutions. These spectra were taken of nondegassed solutions. The singlet-triplet spectrum of 0.15 molal mercuric bromide was also taken with naphthalene as reference and in 5 cm cells.

Table I

EFFECTS OF DEGASSING ON 0.1 M MERCURIC CHLORIDE IN NAPHTHALENE

Sample (times degassed)	Absorbance			
	5500 A	4730 A	4630 A	4430 A
0	0.00	0.113	0.118	0.204
1	0.006	0.112	0.118	0.196
2	0.007	0.135	0.140	0.223
3	-0.010	0.110	0.116	0.195
4	-0.010	0.109	0.115	0.193

Naphthalene Plus Mercuric Acetate

Singlet-triplet spectra were taken of 0.05, 0.10, 0.15, and 0.20 molal solutions of mercuric acetate in naphthalene with air as a reference and 10 cm cells. The solutions were not degassed.

Naphthalene Plus Arsenic Trichloride

Singlet spectra were taken of 1.17, 1.68, and 3.25 molal solutions (non-degassed) of arsenic trichloride in naphthalene in 10 cm cells with air as a

reference. The 1.17 molal solution was degassed one time and the spectrum taken again. This singlet-triplet spectrum did not show any appreciable change in absorption when compared to the spectrum of the nondegassed solution.

Naphthalene Plus Antimony Trichloride

The following singlet-triplet spectra were taken of nondegassed solutions of antimony trichloride in naphthalene: 0.10 m (10 cm cells), 0.20 m (5 cm cells), 0.50 m (5 cm cells), and 1.0 m (1 cm cells). These spectra were taken with air as a reference. A singlet-triplet spectrum of 0.50 molal antimony trichloride was also taken in 5 cm cells with naphthalene as a reference. The 0.50 molal solution was degassed and another spectrum taken (air reference). No change in the intensity of the singlet-triplet band was observed. This 0.50 molal solution was allowed to stand (at ca. 93°C) for ca. 24 hours. Spectra were then taken before and after degassing. These spectra were almost identical, both showing a large increase in absorption in the singlet-triplet region without any increase in the singlet-triplet bands. This increase in absorption was attributed to the formation of another absorbing species when naphthalene and antimony trichloride were heated together.

Naphthalene Plus Bismuth Trichloride

Singlet-triplet spectra of 0.001 m (10 cm cells), 0.002 m (10 cm cells), 0.010 m (1 cm cells), and 0.030 m (1 cm cells) solutions of bismuth trichloride

in naphthalene were taken with air as reference. These spectra were taken of nondegassed solutions. A singlet-triplet spectrum of 0.01 molal bismuth trichloride was taken with naphthalene as a reference (nondegassed sample in 5 cm cells).

Naphthalene Plus Stannic Chloride

Solutions of stannic chloride in naphthalene were bright yellow in color and absorbed strongly in the singlet-triplet region. Because of this, no measurement of singlet-triplet absorption could be obtained.

Naphthalene Plus Lead Chloride

Lead tetrachloride is yellow in color (absorbs strongly in the singlet-triplet region) and could not be used as a heavy-atom perturber.

Lead (II), Zinc, and Cadmium Chloride Plus Naphthalene

Lead (II), zinc, and cadmium chloride are all quite insoluble in naphthalene and did not cause any observable enhancement of the singlet-triplet transitions of naphthalene. The solubilities of zinc and cadmium chloride in naphthalene were checked using EDTA titrations. Eriochrome black T was used as an indicator and the solutions to be titrated were buffered with a pH 10 ammonium buffer. No zinc or cadmium could be detected by this method.

III. SPECTRA OF BENZENE AND BENZENE COMPLEXES

These spectra were taken on either a Beckman DK-2 or a Cary 14 spectrometer using a deuterium light source. Reagent grade benzene and mercuric chloride were used without further purification. Mercuric chloride was the only salt, of the salts tested, that was found suitable as heavy-atom perturber of the singlet-triplet transitions of benzene. Solutions of the other salts (mercuric bromide, thallium chloride, antimony trichloride, and bismuth trichloride) in benzene absorbed light too strongly in the singlet-triplet region of benzene.

Benzene Plus Oxygen

Oxygen was bubbled through benzene for ca. one-half hour and the singlet-triplet spectrum taken in 10 cm cells. Upon bubbling nitrogen through this benzene solution for ca. one-half hour and again taking a spectrum, the singlet-triplet bands disappeared.

Benzene Plus Mercuric Chloride

The singlet-triplet spectrum of 0.02 molar mercuric chloride in benzene was taken in 10 cm cells with benzene as a reference.

IV. SPECTRA OF DIPHENYLMERCURY AND PHENYLMERCURIC ACETATE

The singlet-triplet spectrum of diphenylmercury was taken in chloroform (0.050 molar) with the Beckman DK-2 spectrometer. These spectra were taken in 10 cm cells using chloroform as a solvent. The singlet-triplet spectrum of phenylmercuric acetate was taken in the same manner except that glacial acetic acid was used as the solvent (0.10 molar). In both cases, Eastman chemicals were used without further purification.

The singlet-triplet bands of phenylmercuric acetate (in glacial acetic acid) were shifted ca. 30 A to the blue of the diphenylmercury (in chloroform) bands. To see if this was a solvent effect, the singlet-triplet spectrum of diphenylmercury was again taken in glacial acetic acid. Except for a broadening of the peaks, this spectrum was identical (within experimental error) to the diphenylmercury spectrum in chloroform.

V. INTERPRETATION OF SPECTRA

The interpretation of the singlet-triplet spectra of the naphthalene complexes was complicated by two different factors. First, it was observed that a change in the optical densities of these liquid naphthalene solutions occurred with time. The actual size and shape of the singlet-triplet peaks did not change with time; they were only displaced upward on the chart paper. The second factor affecting these spectra dealt with the positions of the charge-transfer bands of these complexes. The tails of these intense bands, to varying degrees, overlapped the weak singlet-triplet bands.

The singlet-triplet bands appeared on the tails of these charge-transfer bands. In the case of stannic chloride-naphthalene complex, the charge-transfer band completely covered up the singlet-triplet bands (see spectrum no. 8). In the other complexes where at least a portion of the singlet-triplet bands were observable, the contribution of the charge-transfer bands to the optical densities of these complexes (in the singlet-triplet region) could not be determined.

Because of these two factors, meaningful integrated extinction coefficients (as oscillator strengths) could not be obtained for all the complexes studied. However, using several approximations, oscillator strengths were calculated for the singlet-triplet transitions of several of these complexes. The method used will be discussed later. Since oscillator strengths could not be obtained for all the enhanced singlet-triplet bands, a method of comparing

singlet-triplet intensities of these complexes had to be obtained. This method consisted of finding enhancement factors for a series of concentrations of heavy-atom salts in naphthalene.

Calculation of Enhancement Factors

Enhancement factors were obtained in the following manner. Singlet-triplet spectra were taken of several different concentrations of each heavy-atom salt (mercuric chloride, mercuric bromide, mercuric acetate, arsenic trichloride, antimony trichloride, and bismuth trichloride) in naphthalene. The approximate peak heights of the 4730 A peak (of the singlet-triplet transition of naphthalene) were then found for each of the above spectra.

The 4730 A peak was chosen because it was affected less by the positions of the charge-transfer bands of the complexes. The approximate peak heights were then found for each spectrum by assuming that the background peaks (these were combinations of charge-transfer bands and the singlet-singlet band of naphthalene) were straight lines (see figure 4). The center of the 4730 A peak was then found for each spectrum. The spectra were then marked at points 180 A on both sides of the center of the peak. Then, for each spectrum, the absorbance at these two points were averaged and subtracted from the absorbance reading at the center of the peak. These approximate peak heights, obtained from the different spectra, were then corrected so that they were all based on the same pathlength of solution.

These corrected peak heights were then plotted versus concentration of salt for each of the different complexes studied. The slopes of these plots (see figure 5) were the enhancement factors and gave a rough indication of singlet-triplet intensity enhancement ability of each of inorganic salts studied (table II).

Table II

Perturber	Enhancement Factor
$AsCl_3$	$6 \pm 3 \times 10^{-3}$
$Hg(C_2H_3O_2)_2$	$1.56 \pm .2 \times 10^{-1}$
$SbCl_3$	$1.7 \pm .1 \times 10^{-1}$
$HgCl_2$	$2.4 \pm .2 \times 10^{-1}$
$HgBr_2$	$3.1 \pm .2 \times 10^{-1}$
$BiCl_3$	$2.6 \pm .1$

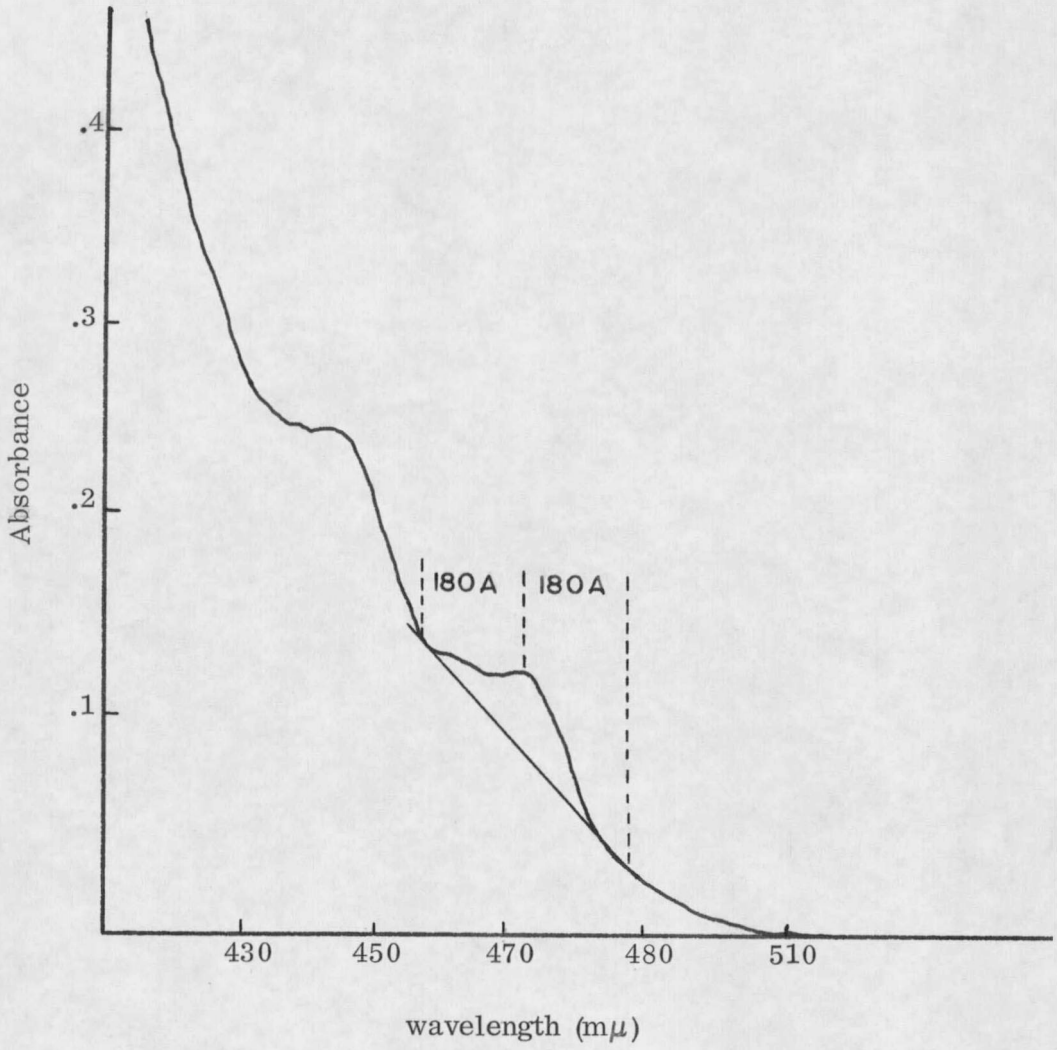


Figure 4. Calculation of enhancement factors (1). This is the spectrum of 0.15 molal solution of mercuric chloride in naphthalene (10 cm pathlength).

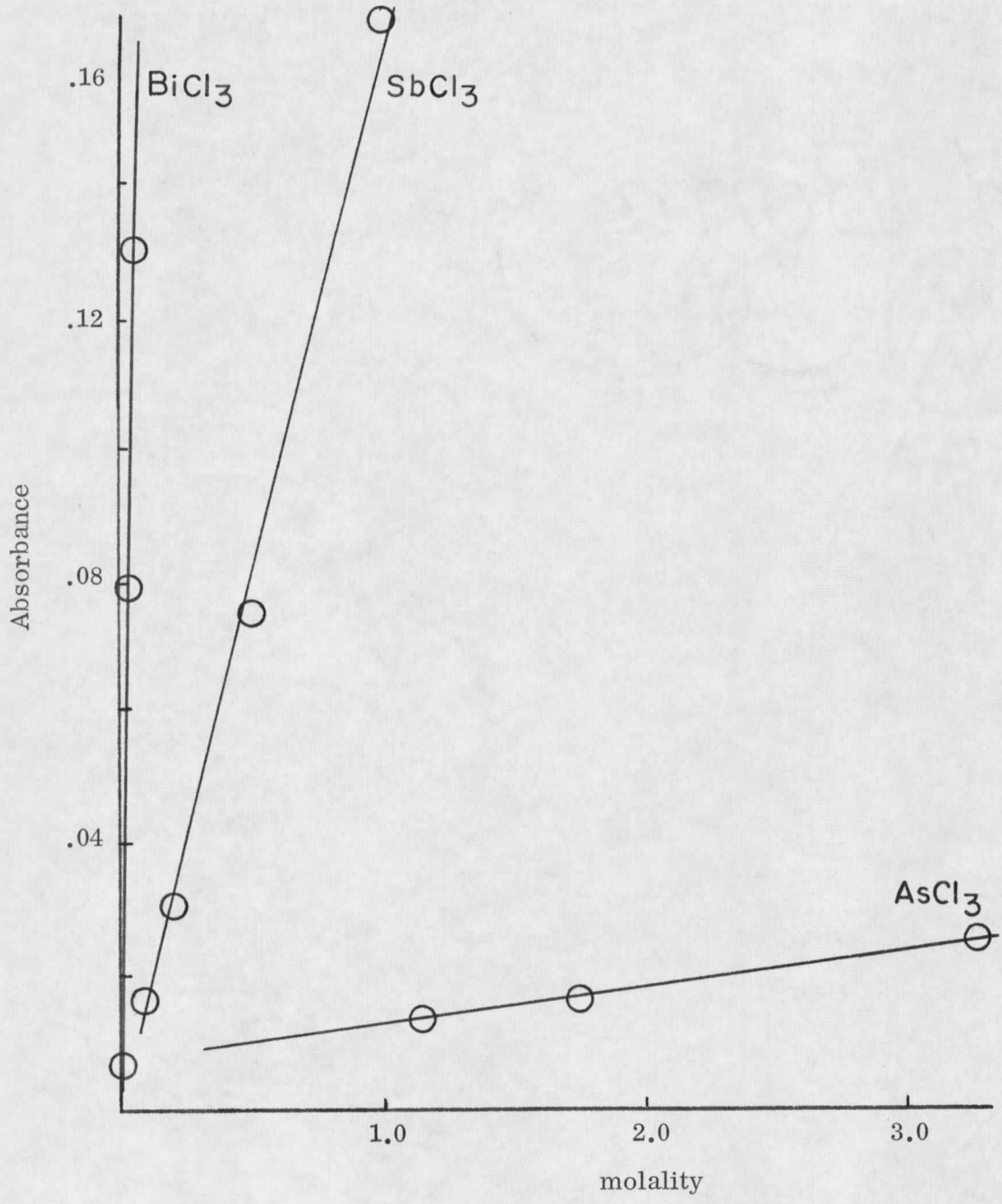


Figure 5. Calculations of enhancement factors (2). Plots of corrected peak heights versus concentrations for $AsCl_3$, $SbCl_3$, and $BiCl_3$ complexes.

Calculation of Oscillator Strengths

Oscillator strengths were calculated using the formula (78),

$$f_{ST} = 4.32 \times 10^{-9} \int \epsilon d\nu$$

The integral in this expression is the integrated molal extinction coefficient. This is the area under the spectral band when the spectrum is plotted as extinction coefficient versus wave numbers. The singlet-triplet bands studied here were located on the tails of intense spectral bands. These intense bands were a combination of the singlet-singlet band of naphthalene and the charge-transfer band of the complex in question. The contribution of the background peak to the absorption was obtained by extrapolating a linear plot of log ϵ versus ν, from shorter wavelengths, where the contribution of the singlet-triplet band is assumed to be negligible. This extrapolated tail is then plotted on the singlet-triplet spectrum and the area between the actual absorption band and this exponential tail is the integrated extinction coefficient (this is only true when the spectrum is plotted in terms of extinction coefficient and wave number).

The area between the curves was obtained using a graphical integration method (54). The following procedure was used. Points were picked at close intervals along the spectrum. These points were recorded in wavelengths and then converted to wavenumbers (ν). The intervals between the points were close enough together so that the spectrum approximated a straight line between the points. For each wavenumber (ν) recorded, the difference between the

absorbance of the original spectrum and the exponential tail (A_{diff}) was found. Next the differences in the wavenumbers ($\Delta\nu$) and the average of the A_{diff} ($\overline{A_{diff}}$) were found for each successive pair of points. The summation of all the products $\overline{A_{diff}}\ \Delta\nu$ was then computed. This result (divided by the factor pathlength times concentration) gave the approximate extinction coefficient.

Table III

OSCILLATOR STRENGTHS FOR SINGLET-TRIPLET TRANSITIONS

Species	Oscillator Strength (f)
$AsCl_3$-$C_{10}H_8$	1.9×10^{-8}
$SbCl_3$-$C_{10}H_8$	9.6×10^{-7}
$HgCl_2$-$C_{10}H_8$	1.2×10^{-6}
$HgCl_2$-C_6H_6	4.4×10^{-6}
$(C_6H_5)_2Hg$	1.5×10^{-5}
$C_6H_5HgOCOCH_3$	7.9×10^{-6}

DISCUSSION

I. LOW TEMPERATURE STUDIES

The purpose of this low temperature work was to test atomic mercury as heavy-atom perturber of the singlet-triplet transitions of certain aromatic compounds (only benzene was used). There were several reasons for testing mercury as a heavy-atom perturber. Mercury is relatively inert, has a high atomic number (Z = 80), and does not absorb light appreciably in the near ultra-violet region of the spectrum. Mercury is also monoatomic in the gas phase and has high enough vapor pressure so that it could be deposited on a cold quartz plate in the manner described in the experimental section.

The spectra of the films of benzene and mercury only showed the 2600 A bands of benzene. No absorption bands were observed in the region of the lowest singlet-triplet transition of benzene. There were several reasons for not being able to observe any enhancement of the lowest singlet-triplet transition of benzene. First of all, the films of benzene and mercury could not be made very thick. Only very thin films had reasonable optical properties, and the thicker films were opaque to light. Because of this, the instruments used in attempting to detect these weak transitions were not sensitive enough. Also a deuterium lamp was used in these experiments; a brighter light source would have allowed thicker films to be used.

Very thin films of mercury were opaque to light. Because of this, the

concentration of mercury in the films had to be kept small (less than ca. 5%). The ideal situation for the most efficient enhancement would occur when each benzene molecule was surrounded by the heavy mercury atoms. When the films contained less than 5% mercury, only a few of the benzene molecules in the film had mercury atoms as nearest neighbors. Since there must be some mixing of the orbitals of the perturbing atom and the perturbed molecule, this did not lead to very efficient enhancement of the singlet-triplet transitions of benzene. Thus very thick films (which would be opaque) would have to be used to observe any enhancement of the singlet-triplet transitions in benzene by this method.

II. DISCUSSION OF SPECTRA

Oxygen Enhanced Singlet-Triplet Spectrum of Naphthalene

The spectrum of a saturated solution of oxygen in liquid naphthalene (spectrum no. 1) showed weak absorption bands in the 4000-5000 A region of the spectrum. These bands disappeared when the solution was degassed, and they were interpretated as being the oxygen enhanced singlet-triplet bands of naphthalene. The oxygen (paramagnetic) enhancement of singlet-triplet transitions has been well characterized (1, 17, 19, 20-26, 43, 47, 70, 80) and has been used as a strong criterion for the location and assignment of triplet states (52, 76). As further evidence of this assignment, these oxygen enhanced bands correspond to those reported in the literature as being caused by a spin forbidden electronic transition from the singlet ground state to the first excited triplet state of naphthalene ($^3B_{2u} - {}^1A_{1g}$) (24, 40, 50, 65).

The spectra of the solutions of naphthalene with mercuric chloride, mercuric bromide, mercuric acetate, arsenic trichloride, antimony trichloride, and bismuth trichloride contained weak absorption bands that corresponded to the oxygen enhanced bands. These bands did not disappear upon degassing and were also interpretated as being due to the $^3B_{2u} - {}^1A_{1g}$ transition of naphthalene. The enhancement of these singlet-triplet bands was explained as being due to a heavy-atom perturbation caused by the heavy metal salts.

Spectra of Complexes of Mercuric Chloride, Bromide, and Acetate

The spectra of solutions of these salts in naphthalene had absorption bands at 473, 462, 443, 434, and 417 mμ (the 417 band was a shoulder that was not observed in the mercuric bromide spectrum). These bands corresponded fairly closely to the reported bands for the lowest singlet-triplet transition of naphthalene (60). Degassing of these solutions did not cause any appreciable change in the intensities of the bands. Referring to table I (degassing data for mercuric chloride solutions), the absorbance reading for the 473 band only changed ca. 1% after the first degassing and the total change in absorbance after four degassings was only ca. 4%. This 4% change is well within the uncertainty of the absorbance readings (ca. 8%).

Table I also shows an abnormal reading after the second degassing. This reading was taken after the solution was allowed to stand heated overnight. The absorbance reading returned to its original value after the solution was again degassed. It was suspected that chlorine gas was formed by a disproportionation reaction of the mercuric chloride. The presence of this gas in solution would cause an increased absorption that should disappear upon degassing.

The optical density of the mercuric acetate solution also increased with time. This increase was more rapid than that for the mercuric chloride solution. Furthermore, the increase in optical density of this solution did not diminish with degassing. This fact seemed to indicate that another absorbing

species (not gaseous) was being formed. This would probably be some sort of substitution compound of naphthalene.

Spectra of Complexes of Arsenic, Antimony, and Bismuth Trichloride

Absorption bands were observed at 473, 462, 443, and 417 mμ in the singlet-triplet spectra of arsenic trichloride and antimony trichloride complexes. Due to the position of the charge-transfer band in the bismuth trichloride complex only the 473 band (shoulder) was observed. For all three of these complexes the optical density in the singlet-triplet region of the spectrum of the heated solutions changed with time. The actual intensities of the singlet-triplet bands did not seem to change, only the base lines of the spectra were displaced upward. Degassing did not have any effect on these increases in absorption. These increases in optical densities were interpreted as being caused by the formation of new absorbing species. The nature of these species was not determined.

Spectra of Diphenylmercury, Phenylmercuric Acetate, and the Mercuric Chloride-Benzene Complex

The singlet-triplet transitions of diphenylmercury, phenylmercuric acetate, and the mercuric chloride-benzene complex appeared as bands on the tails of intense singlet-singlet bands. The spectra of diphenylmercury and phenylmercuric acetate were taken in chloroform and glacial acetic acid, respectively. These solvents were chosen because of solubility requirements. The singlet-

triplet bands of diphenylmercury appeared at the same positions as those reported by Marchetti and Kearns (65) using a phosphorescence excitation technique. Also these bands were located at the same positions as La Paglia (55) reported for the singlet-triplet bands of tetraphenyl lead (also in chloroform).

The singlet-triplet bands of phenylmercuric acetate appeared shifted ca. 30 A to the blue from the diphenylmercury bands (see table IV). The singlet-triplet spectrum of diphenylmercury in glacial acetic acid was almost identical (except for considerable broadening of the bands) to the spectrum in chloroform. This seems to indicate that the spectral shift of the phenylmercuric acetate bands was not a normal solvent shift.

Table IV

POSITIONS OF ENHANCED SINGLET-TRIPLET BANDS OF BENZENE

System	Band positions (mμ)				
Benzene + oxygen		ca. 312	320	330	340
Benzene + mercuric chloride			ca. 320	330	340
Diphenylmercury[a]	305	314	322	331	342
Phenylmercuric acetate[b]	ca. 305	312	318	328	338

[a]chloform solvent, [b]glacial acetic acid solvent

A possible explanation of this spectral shift can be obtained with the help of the molecular orbital diagram in Figure 6. The first singlet-singlet and

singlet-triplet bands of diphenylmercury are shifted to the red of the bands in benzene. This shift can be explained by a resonance effect in diphenylmercury. This resonance (mesomeric) effect interaction causes a splitting of the excited states of diphenylmercury which leads to excited states of lower energies. This leads to a red shift in the observed bands.

The spectrum of the phenylmercuric acetate is complicated by the fact that the first singlet-singlet band is lowered in energy while the first singlet-triplet is raised in energy (again compared to benzene). The shift in the singlet-singlet band can be explained in the following manner. The first excited singlet state is stabilized (lowered in energy) by the delocalization of the pi-electrons of the phenyl ring on to the mercury ion. This delocalization of electrons can also cause the energy difference in the first excited singlet state and the first excited triplet state to be less since electron repulsion would be less in the more delocalized system. The observed spectral shift of the singlet-triplet bands could possibly be due to this lessening of electron repulsion, but more experimental data is needed before this question can be settled.

The singlet-triplet bands in the oxygen and the mercuric chloride enhanced systems were located at the same positions. Degassing had no effect on the mercuric chloride enhanced bands, while the oxygen enhanced bands disappeared upon degassing.

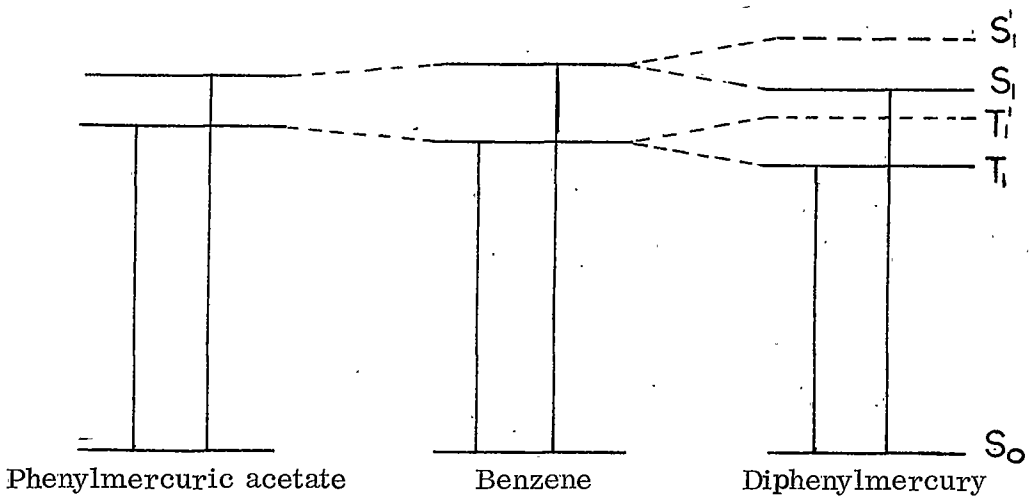


Figure 6. Molecular orbital diagram representing the first singlet-singlet and the first singlet-triplet transitions of benzene, diphenylmercury, and phenylmercuric acetate. The arrows represent observed transitions.

III. DISCUSSION OF NAPHTHALENE COMPLEXES

Solutions of liquid naphthalene with certain inorganic salts (mercuric chloride, mercuric bromide, mercuric acetate, arsenic trichloride, antimony trichloride, bismuth trichloride, and stannic chloride) were yellow in color and absorbed strongly in the near ultra-violet region of the spectrum. The color of these solutions ranged from bright yellow for bismuth trichloride and stannic chloride to pale yellow for the arsenic trichloride solution. These colors were attributed to two factors: the enhanced singlet-triplet transition of naphthalene and the formation of charge-transfer complexes.

These charge-transfer complexes were characterized by the appearance of intense charge-transfer bands. The exact positions of these bands could not be determined since both naphthalene and some of the inorganic salts absorbed strongly in the spectral region where the charge-transfer bands appeared. The relative positions of these bands were obtained from the singlet-triplet spectra by considering the wavelengths where the absorbance readings were equal to one. The following order was obtained (increasing energy of the charge-transfer band from left to right): stannic chloride < bismuth trichloride < mercuric bromide < mercuric chloride < antimony trichloride < mercuric acetate < arsenic trichloride. Since the charge-transfer bands are not the only contributing factors to the optical densities in this region, this order of charge-transfer band energies cannot be considered absolute.

The energy of a charge-transfer complex can be approximated by the expression (2)

$$E_{CT} = I_D - E_A - W$$

For these naphthalene complexes, the electron affinities of the acceptor (E_A) and the coulombic term (W) are not known. For a series of 18 iodine complexes, Briegleb and Czekalla (6) found that W was constant. There does not seem to be any evidence in the literature that W will be constant for a series of complexes with the same donor. Since E_A is not known for any of the acceptors, the nature of W for these naphthalene complexes could not be ascertained. Even with the nature of W unknown, the energy of these charge-transfer complexes should be directly related to the electron affinities of the acceptors. Thus the order of electron affinities should be the same as the order that was observed for the energies of the charge-transfer bands.

The order of electron affinities (more accurately, the acceptor strengths) of these inorganic salts may be discussed in terms of soft acids and bases (induced polarizing abilities) (74, 75). The concept of hard and soft acids and bases is based on experimental observations. It has been found that certain cations (hard acids) form the most stable compounds with the lightest members of a group (hard bases). Other cations (soft acids) form the more stable compounds with the heavier members of a group (soft bases). In hard acids and bases the main interactions are electrostatic in nature. Polarization effects

are more prominent in the soft acids and bases.

Soft bases are characterized by relatively high energy filled orbitals that are easily polarized. Naphthalene and benzene are included in this category. Soft acids are molecules or cations that are usually large in size and are easily polarized. The strength of these soft acids usually increases as you go down a certain group. For the group 5a plus three ions, this order would be: Bi(III) > Sb(III) > As(III). This should also be the order of the trichlorides of this group as electron acceptors.

Both the acetate and the chloride ions are hard bases (acetate > chloride) and should decrease the soft character of the mercury (II) ion. On the other hand, the bromide ion should increase the soft character of the mercury (II) ion. From these soft acid considerations, the following orders of electron acceptors can be obtained.

$$BiCl_3 > SbCl_3 > AsCl_3 \quad \text{and} \quad HgBr_2 > HgCl_2 > Hg(C_2H_3O_2)_2$$

The mercury salts and the tin salt should have considerable soft character, but their relative positions in the order of electron acceptors cannot be predicted from the known data on soft acids.

IV. THE NATURE OF CHARGE-TRANSFER INTERACTIONS

Bonding interactions in charge-transfer complexes are classified as charge-transfer forces and classical electrostatic forces (these include dipole-dipole and dipole-induced dipole interactions). Mulliken (68), in his original treatment of these complexes, assumed that the charge-transfer forces would be predominant. In a later publication (69), Mulliken has questioned this assumption and pointed out the evidence in support of the importance of classical interactions in the energy of charge-transfer complexes. Several authors (15, 39, 64) have indicated a belief in the preponderance of Coulomb and polarization (dipole-dipole and dipole-induced dipole) forces in the stability of charge-transfer complexes, especially those of pi-pi nature. Pure quadrupole resonance spectroscopy data (45) and data on the Br-Br interatomic distances (41), for the benzene-bromine complex in the solid state, indicates that the amount of charge-transfer to the bromine is very small.

The nature of the bonding interactions in the complexes studied here can be examined by considering the changes in the bond lengths in complexed naphthalene (from the crystal structure of the antimony trichloride-naphthalene complex as reported by Hulme and Szymanski (48)) from that of pure crystalline naphthalene (10). Since bond lengths are related to bond orders, these bond orders were calculated and compared for both cases of bonding in naphthalene.

The bond order (n) for a particular bond is related to the number of electrons associated with that bond. Pauling (73) used the following formula to relate these bond orders to the lengths of the bonds (bonds must be of a similar type).

$$D(n) = D_1 - 0.71 \log n$$

Here D(n) is the experimental bond length and D_1 is a corrected single bond length (1.504 A). Using this formula and the bond lengths from X-ray crystal structure data (10, 48), bond orders for the crystalline antimony trichloride-naphthalene complex and for crystalline naphthalene were calculated and compared (table V).

Table V

Bond lengths and bond orders for naphthalene and complexed naphthalene (see figure 1).

Bond	1	2	3	4	5	6
D(n) naphthalene	1.420	1.359	1.395	1.359	1.420	1.395
n naphthalene	1.30	1.60	1.43	1.60	1.30	1.43
D(n) complex	1.44	1.42	1.34	1.31	1.42	1.43
n complex	1.23	1.31	1.70	1.88	1.31	1.27

The calculated bond orders show a shift of electron density to bonds 3 and 4 (the region in which the naphthalene is weakly bonded to the antimony

trichloride molecule). Comparing the bond lengths and bond orders for pure naphthalene and naphthalene in the complex, there seems to be little or no significant shift of electrons out of the pi-system of the naphthalene to the antimony trichloride molecule.

Thus it seems reasonable to assume that the bonding in the antimony trichloride-naphthalene complex is principally a classical electrostatic interaction (dipole-induced dipole). Since all the naphthalene complexes studied here are of a similar nature, it is expected that the principal bonding interaction in these complexes is of the dipole-induced dipole type. There may be more charge-transfer interactions in the stronger complexes (stannic chloride and bismuth trichloride), but this should account for very little of the bonding even in these complexes.

IV. SINGLET-TRIPLET ENHANCEMENT

The effectiveness of an acceptor as a heavy-atom perturber was determined by means of enhancement factors and oscillator strengths (see experimental section). This order for this effectiveness was found to be: bismuth trichloride > mercuric bromide > mercuric chloride > antimony trichloride ≈ mercuric acetate > arsenic trichloride. It is generally agreed that this heavy-atom effect is of a spin-orbit nature. This spin-orbit nature is observed when comparing the spin-orbit constants (ζ) with the enhancement factors (see table VI). Except for the case of the mercuric acetate complex, the enhancement factors increase with increasing ζ.

Table VI

Comparison of heavy-atom perturbers

	Enhancement factor	Oscillator strength	ζ
$AsCl_3$	$6 \pm 3 \times 10^{-3}$	1.89×10^{-8}	1960
$Hg(C_2H_3O_2)_2$	$1.56 \pm .2 \times 10^{-1}$		6080
$SbCl_3$	$1.7 \pm .1 \times 10^{-1}$	9.55×10^{-7}	4380
$HgCl_2$	$2.4 \pm .2 \times 10^{-1}$	1.19×10^{-6}	6080
$HgBr_2$	$3.1 \pm .2 \times 10^{-1}$		6080
$BiCl_3$	$2.6 \pm .1$		13900

The effectiveness of an acceptor as a heavy-atom perturber also increases with the strength of the charge-transfer complex formed. The enhancement factor for the mercuric bromide complex is about double that for the mercuric acetate complex. This increase in enhancement is attributed to the higher electron affinity (forms a stronger charge-transfer complex) of mercuric bromide. It is assumed here that the heavy metal of the salt makes the principal contribution to the spin-orbit coupling. This may not be entirely true and some of the effect observed here may be due to the bromine atoms. This same effect is observed when one compares the enhancement factors for mercuric acetate and mercuric chloride. Here the relatively light chlorine atoms should not contribute much to the spin-orbit coupling.

In unperturbed naphthalene, singlet-triplet transitions are made slightly allowed through the mixing (spin-orbit) of excited singlet and triplet states (by stealing intensity from singlet-singlet and triplet-triplet transitions). The amount of mixing is inversely proportional to the difference in energy of the two states. In a heavy-atom perturbed molecule, it is also expected that the singlet-triplet transition will gain intensity through the mixing of electronic states. But in the perturbed system, one must also consider the mixing of the excited states of naphthalene with the excited states of the heavy-atom perturber. As discussed previously, it is theoretically predicted that this mixing may occur by two different mechanisms (charge-transfer and exchange). The singlet-triplet

intensity predicted by both of these mechanisms depends on the fourth power of the overlap integral between the orbitals of the heavy-atom perturber and the naphthalene molecule. Because of this one must assume that both of these mechanisms contribute to the intensity of the charge-transfer transitions.

There are several factors that indicate that the charge-transfer mechanism will be most important in the systems studied here. First of all, it was found that the singlet-triplet enhancement increases with increasing strength of the complex. Second, all the complexes examined here have intense charge-transfer bands in the region of the first singlet-singlet band of naphthalene. These charge-transfer states should have much of the character of the excited states of the heavy-atom perturbers (large spin-orbit coupling). This should lead to considerable mixing (spin-orbit) of the excited states of naphthalene (both singlet and triplet) with these charge-transfer states (see figure 4). This spin-orbit mixing process will steal intensity from the charge-transfer transitions. In the exchange mechanism, only the mixing of the orbitals of the heavy-atom perturber and the naphthalene molecule is considered. The possibility of stealing intensity from the intense charge-transfer transitions is not considered. These considerations are supported by similar arguments for the charge-transfer mechanism in the enhancement of singlet-triplet transitions of aromatic compounds by heavy-atom solvents (63).

Assuming that charge-transfer is the principal source of singlet-triplet enhancement in these complexes, the way in which the intensity is borrowed

from the charge-transfer transitions is summarized in figure 7. The representation of the electronic states in this figure is an oversimplification. The states represented as pure donor and acceptor states really have some charge-transfer character in them. This is due to the mixing of these states with the charge-transfer states. In the complexes studied here, the amount of charge-transfer character in the first triplet state of naphthalene seems to be small since there is little change in the positions of the observed singlet-triplet bands compared to the bands in the unperturbed molecule.

Since the amount of mixing is inversely proportional to the difference in energy of the two states, there will be more mixing of the naphthalene triplet state with the first excited charge-transfer state in the stronger complexes. Thus the stronger the charge-transfer complex the more enhancement of the donor singlet-triplet transition is expected (this is only true for acceptors with comparable spin-orbit coupling). The observed enhancement of the singlet-transitions agrees with this expected trend.

Benzene Systems

The intensity of the diphenylmercury singlet-triplet band is approximately double that of phenylmercuric acetate (see table III). The difference in intensities is explained by the presence of two benzene rings in the diphenylmercury system. Considering that the spin-orbit coupling in the mercury atom should be the primary factor affecting these intensities, this result is to be expected.

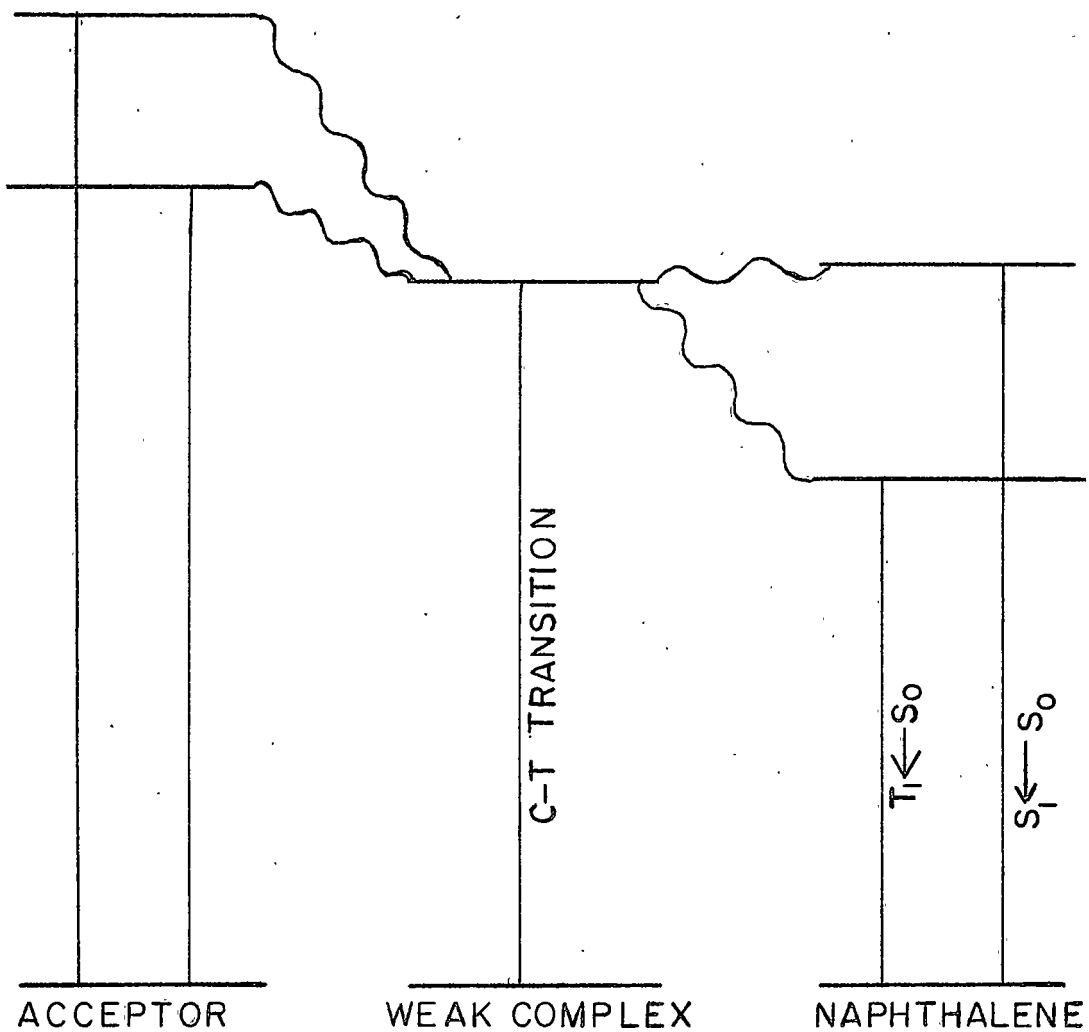


Figure 7. The manner in which singlet-triplet transitions may steal intensity from a charge-transfer transition. The arrows represent observed transitions and the wavy lines indicate a spin-orbit interaction between two states.

The intensity of the mercuric chloride enhanced bands are approximately half that of the phenylmercuric acetate bands. This difference is probably due to different amounts of mixing of the mercury (or mercury chloride) states with the π-states of benzene.

In the mercuric chloride-benzene complex, the mixing of these states most likely occurs by a charge-transfer mechanism (same arguments apply here as did for the haphthalene complexes). The mixing of electronic states of benzene and mercury in the covalently bonded compound will probably involve mixing with intermediate states. The sigma bonded mercury should lead to more overlap of the orbitals of the benzene molecule and the mercury atom. Considering this alone, the covalently bonded mercury should cause more enhancement of the benzene singlet-triplet transitions than the charge-transfer bonded mercury.

APPENDIX A

Calculation of Spin-Orbit Constants

Spin-Orbit Coupling Constants

The approximate values of the spin-orbit coupling constants were obtained using the Lande interval rule (9). This rule states that the interval between two adjacent energy levels of an atomic state (term) is proportional to the higher J value of the two terms. In the first approximation, this constant is the spin-orbit coupling constant. The approximate spin-orbit coupling constants (ζ) were obtained from the multiplet spacings in the P-states of the metal atoms of the various salts. These multiplet spacings were obtained from a compilation of atomic energy levels by Moore (67). The spin-orbit coupling constant is the observed multiplet spacing divided by J. These multiplet spacings and the observed spin-orbit coupling constants for these P-states are tabulated in table VII.

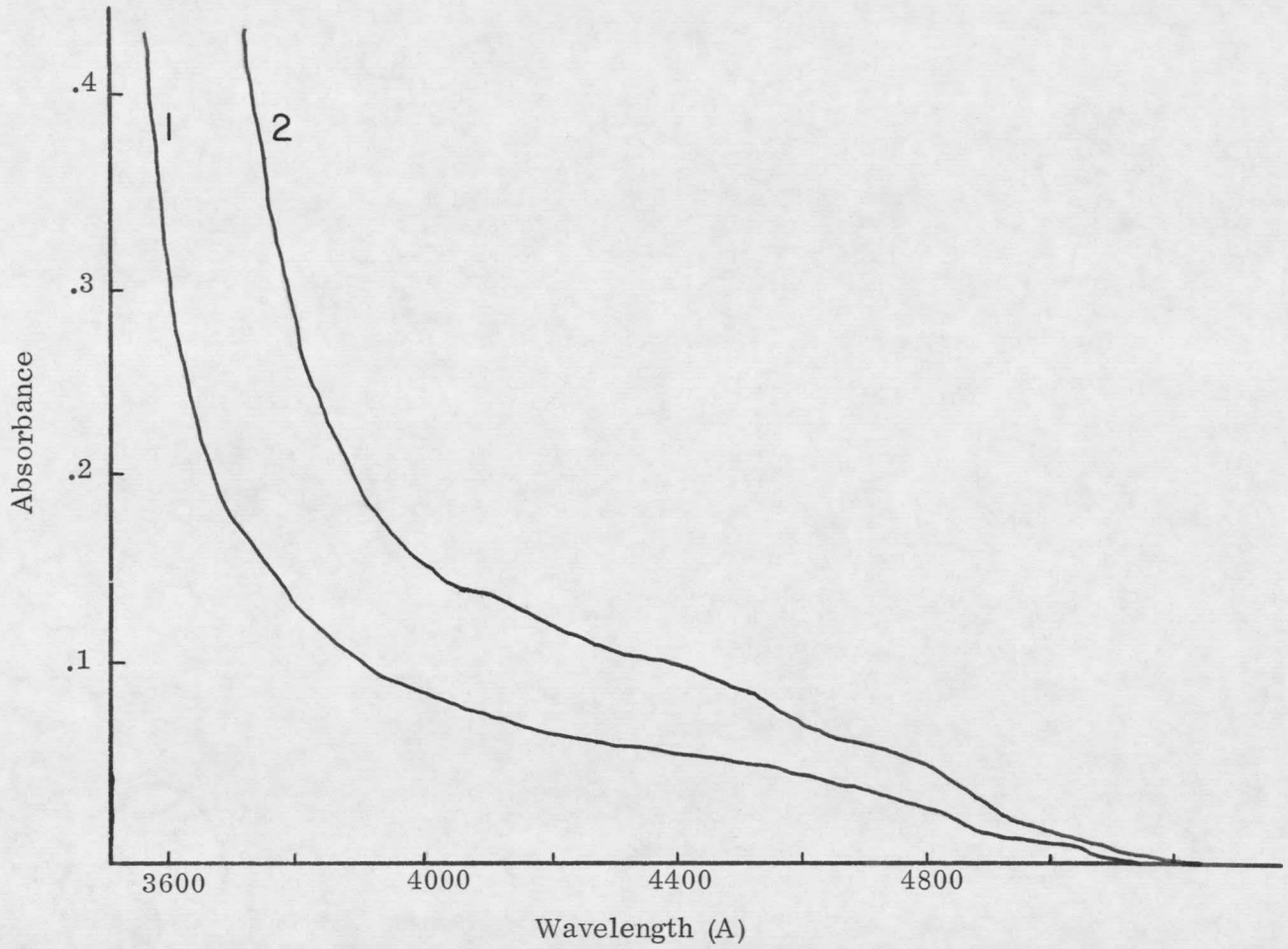
Table VII

TABULATION OF SPIN ORBIT COUPLING CONSTANTS AND MULTIPLET SPACINGS

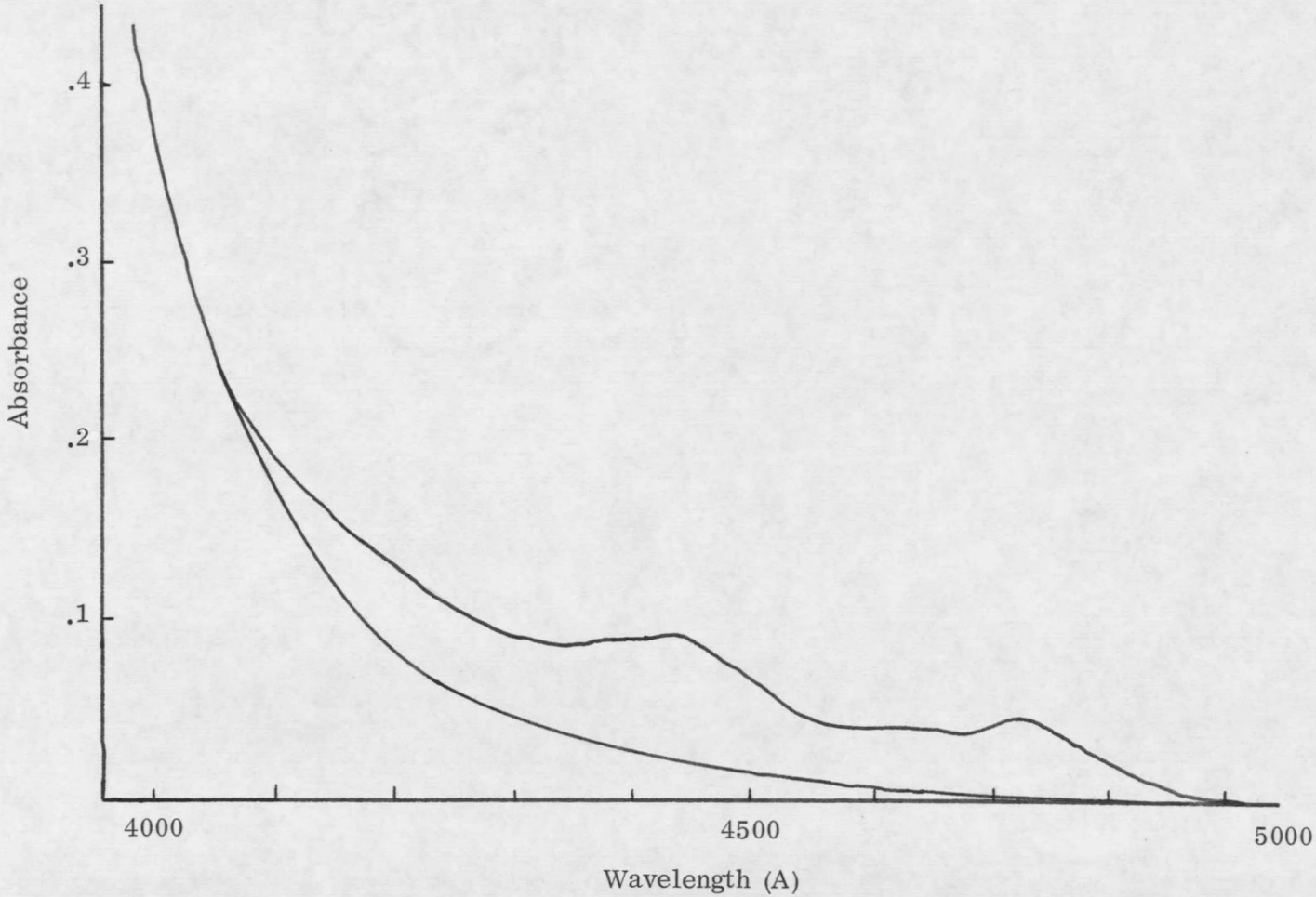
Ion	Level	J	Energy (K)	Interval	ζ(K)
Zn(II)	^2P	1/2	48480	788	3583
		3/2	49354		
Cd(II)	^2P	1/2	44136	2482	1650
		3/2	46618		
Hg(II)	^2P	1/2	51485	9183	6080
		3/2	60608		
AS(III)	^2P	1/2	0.000	2940	1960
		3/2	2940		
Sb(III)	^2P	1/2	0.000	6576	4380
		3/2	6576		
Bi(III)	^2P	1/2	0.000	20788	13900
		3/2	20788		
Sn(IV)	^2P	1/2	0.000	6508	4340
		3/2	6508		

APPENDIX B

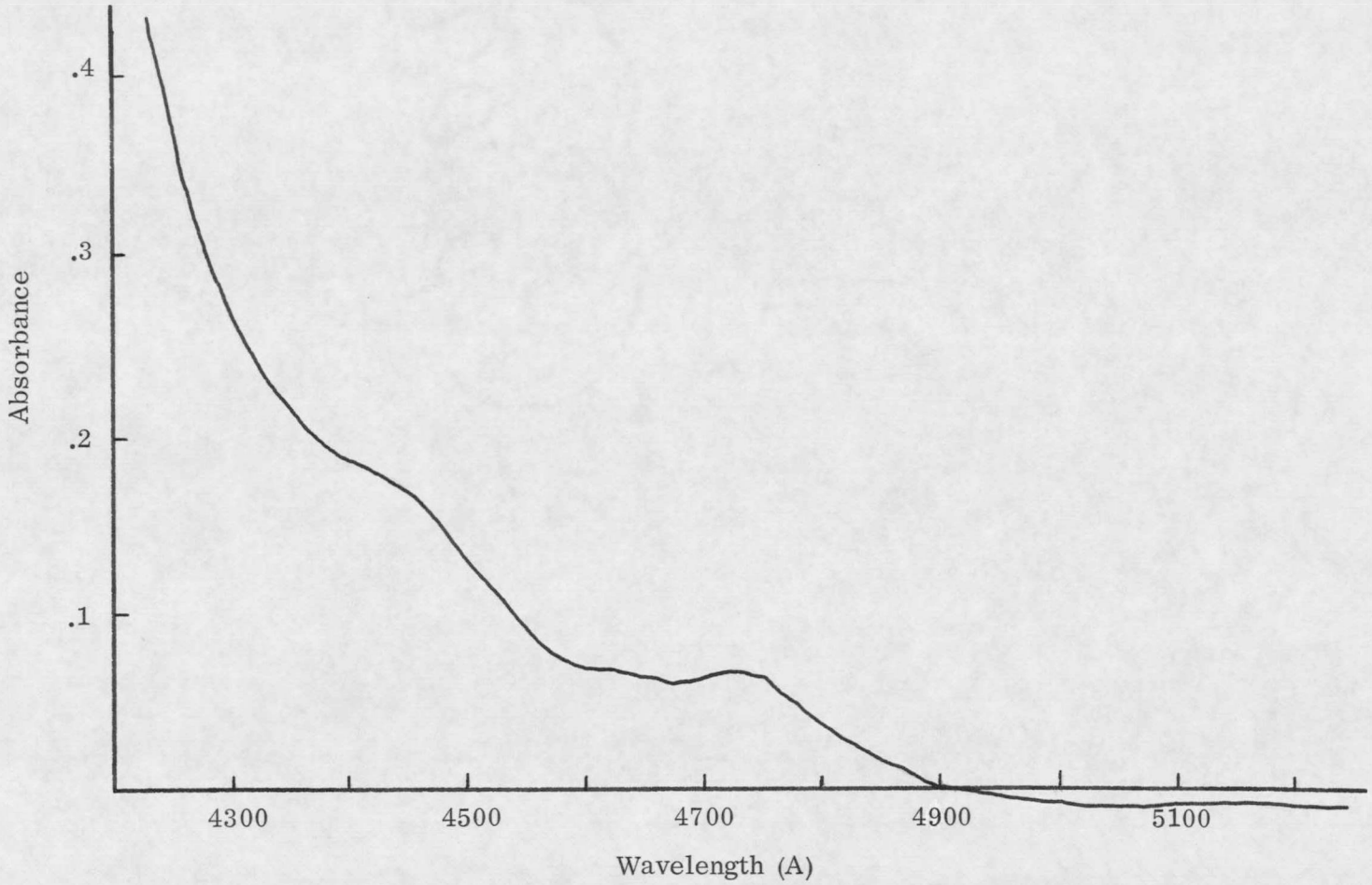
Singlet-Triplet Spectra



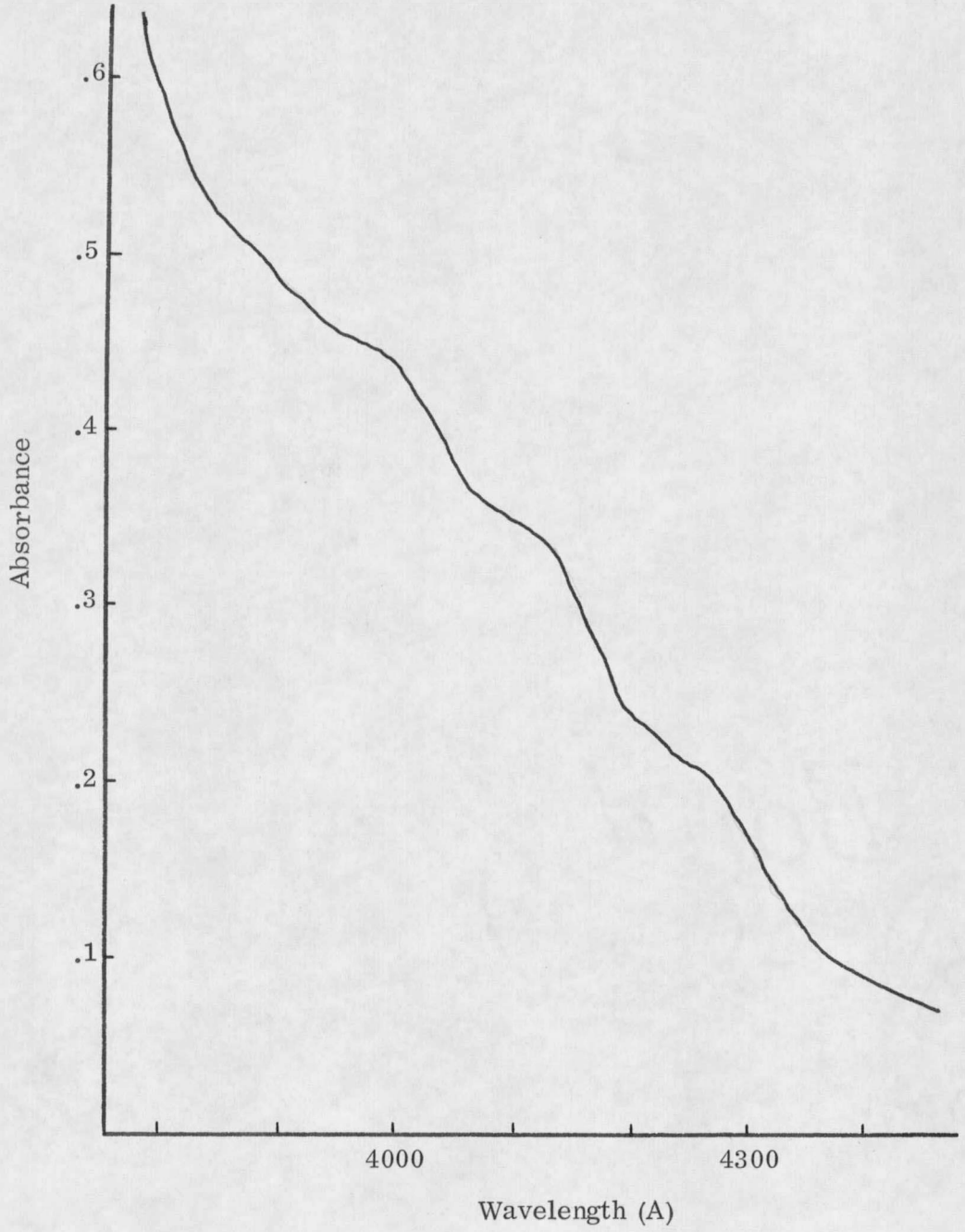
Spectrum No. 1. (1) Degassed naphthalene in 10 cm cells, reference air. (2) Naphthalene plus oxygen in 10 cm cells, reference air.



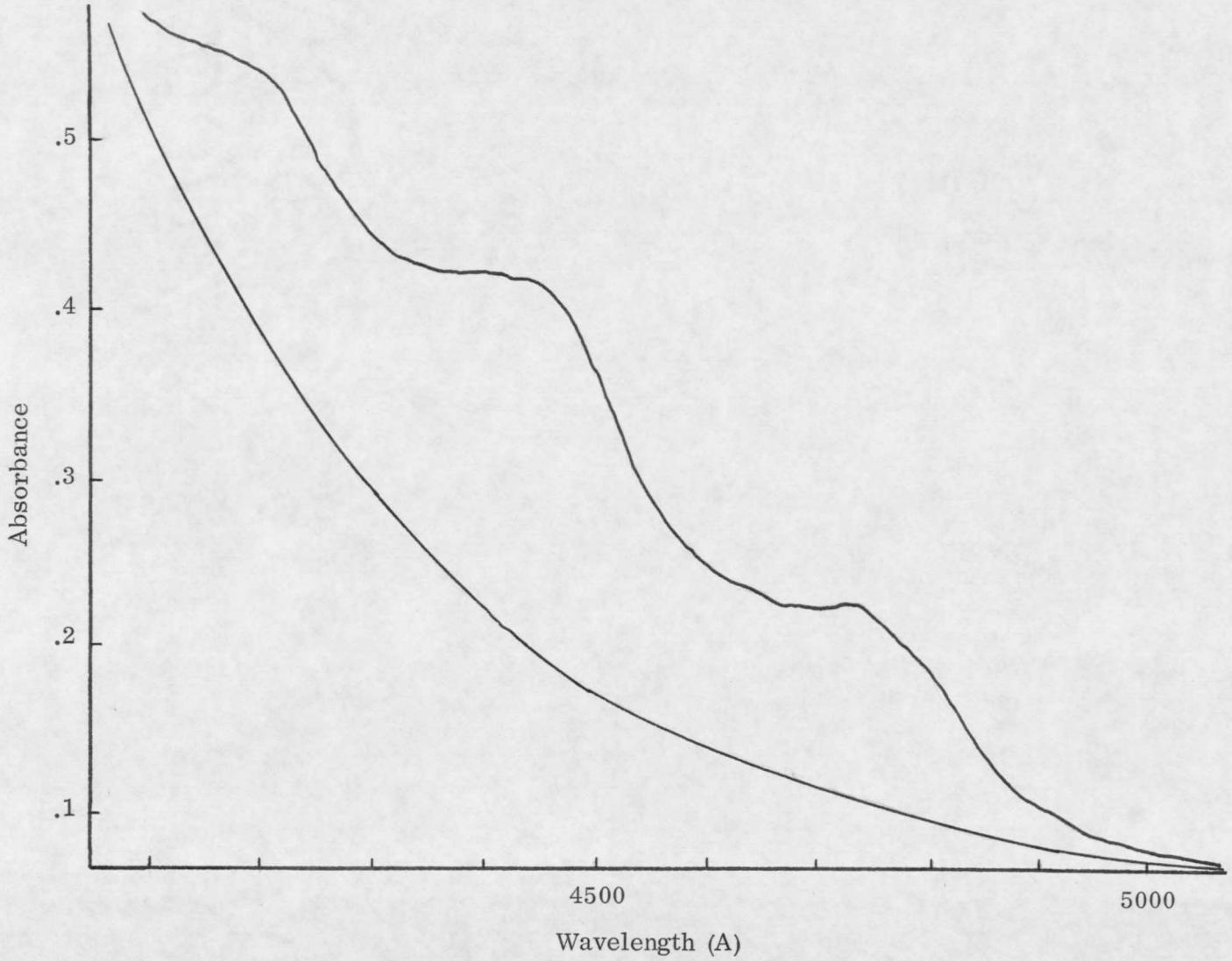
Spectrum No. 2. 0.15 molal mercuric chloride in naphthalene, 5 cm cells, reference naphthalene



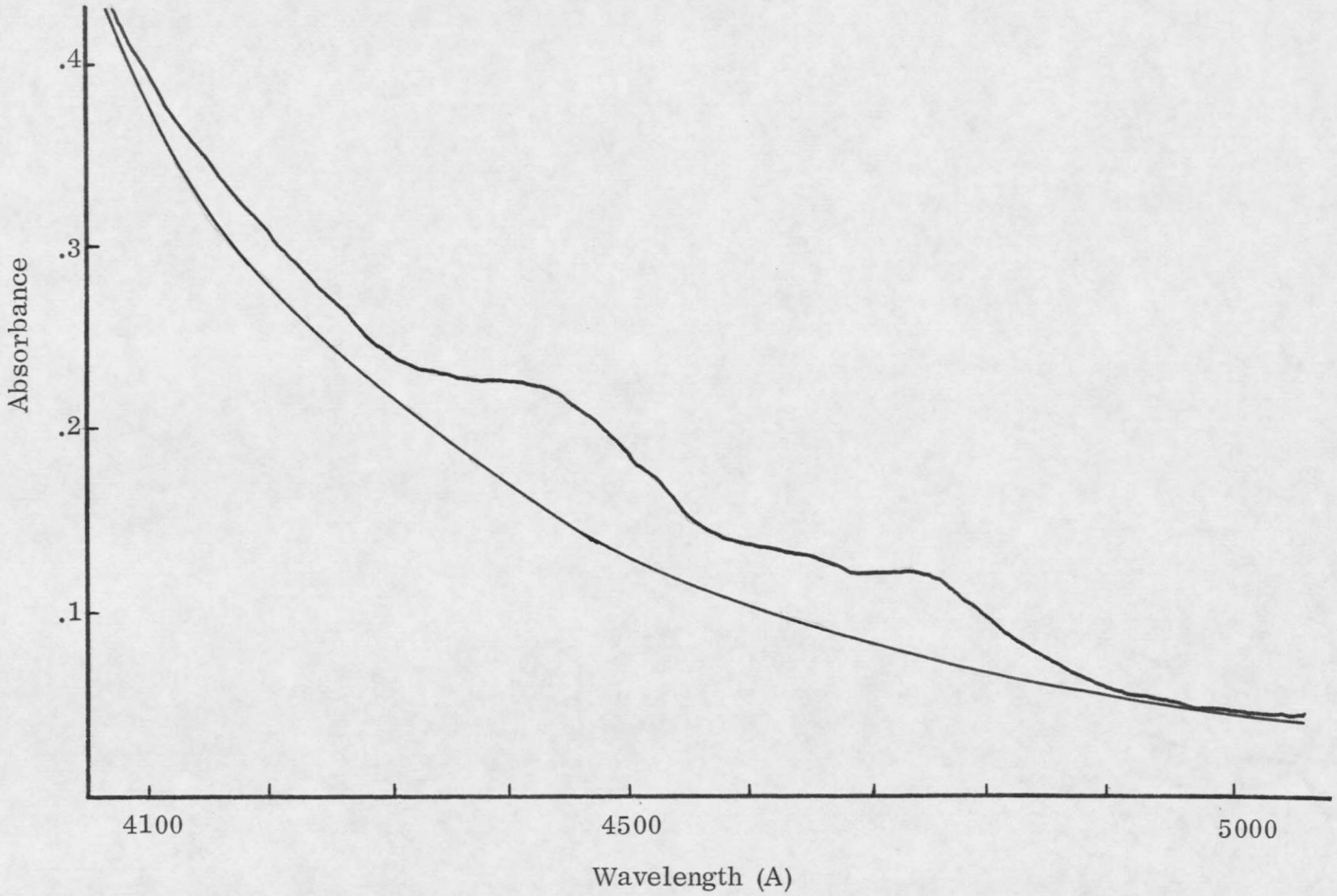
Spectrum No. 3. 0.15 molal mercuric bromide in naphthalene, naphthalene reference, 5 cm cells.



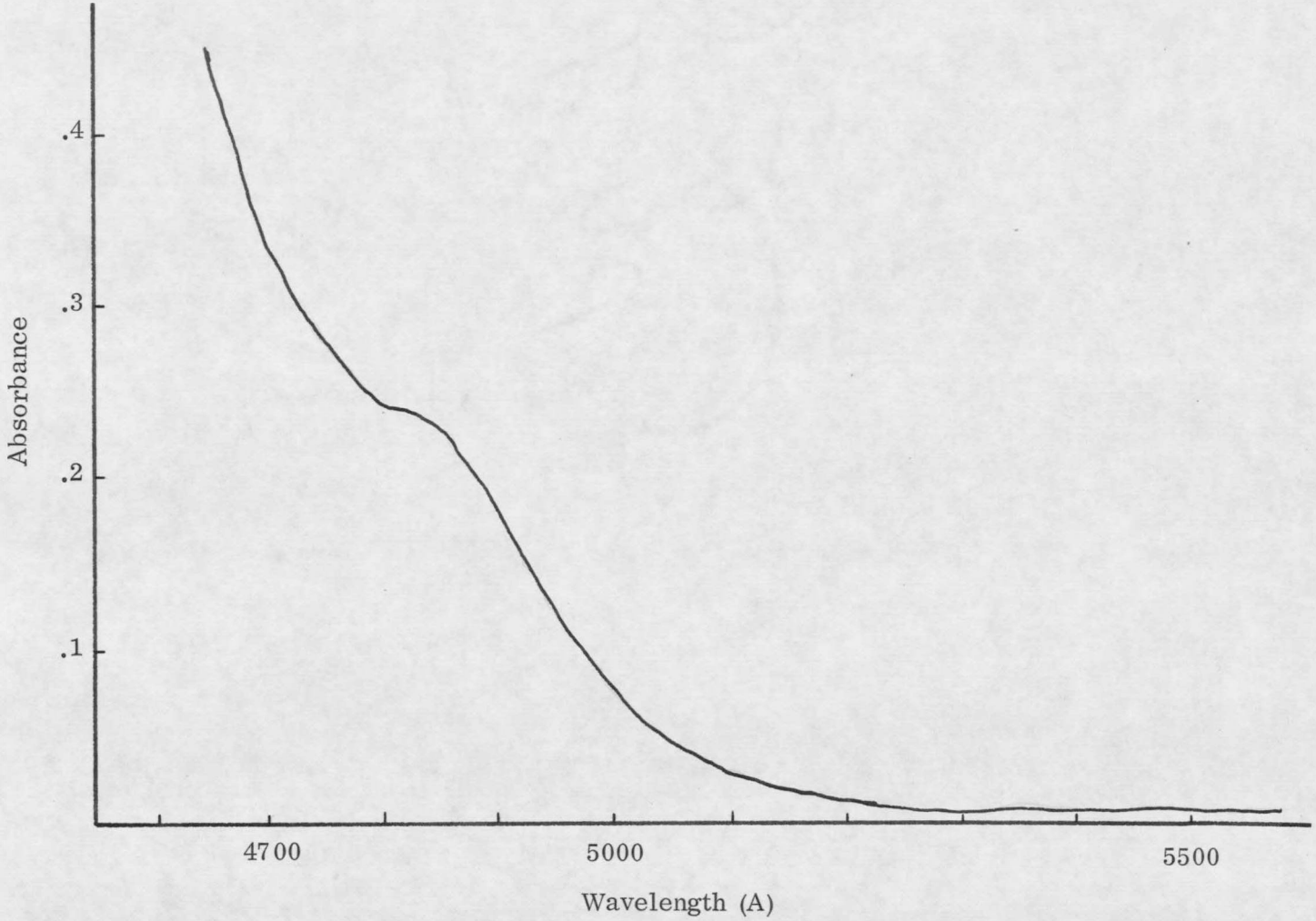
Spectrum No. 4. 0.10 molal mercuric acetate in naphthalene, 10 cm cells, air reference.



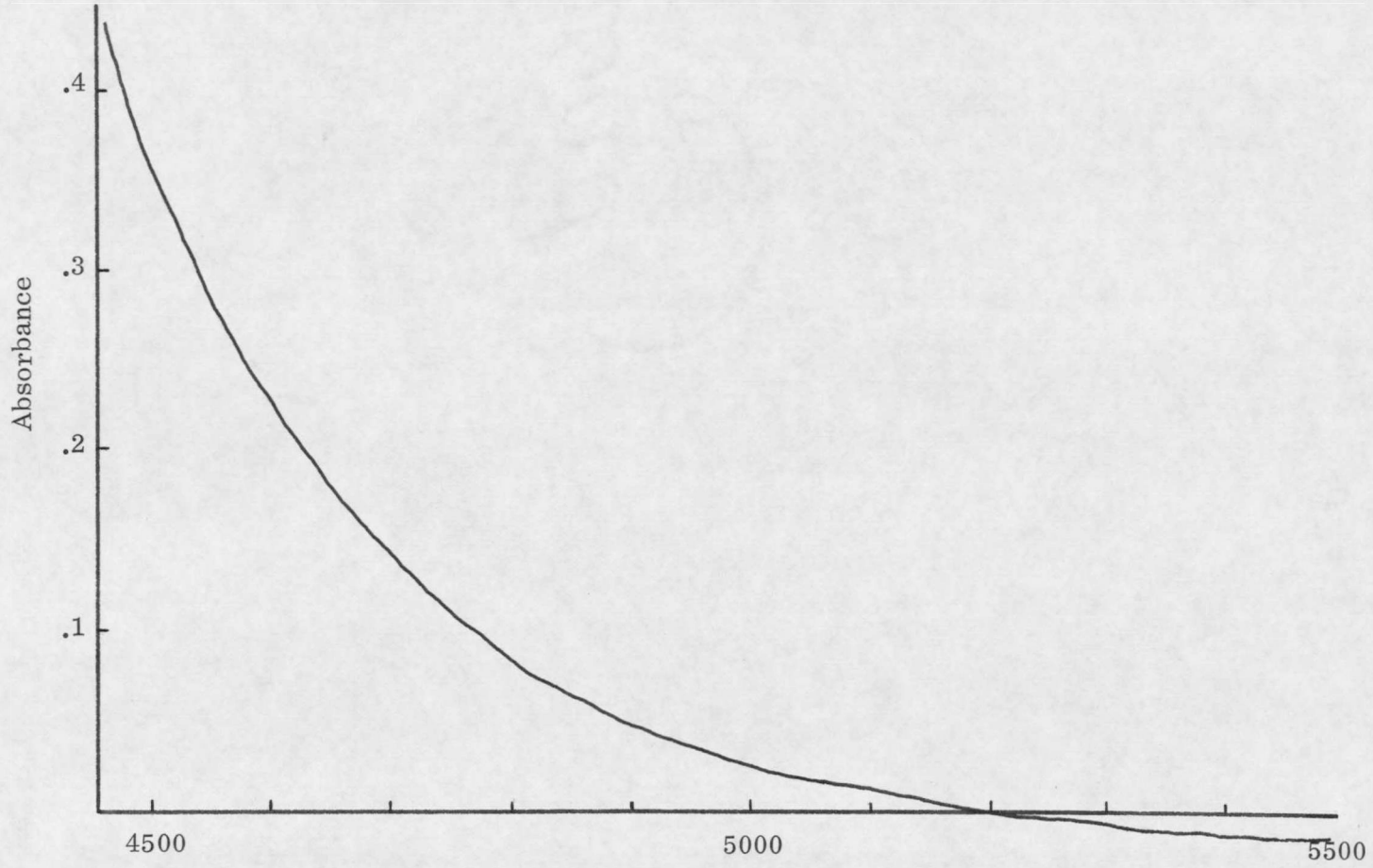
Spectrum No. 5. 0.50 molal antimony trichloride in naphthalene, naphthalene reference, 5 cm cells.



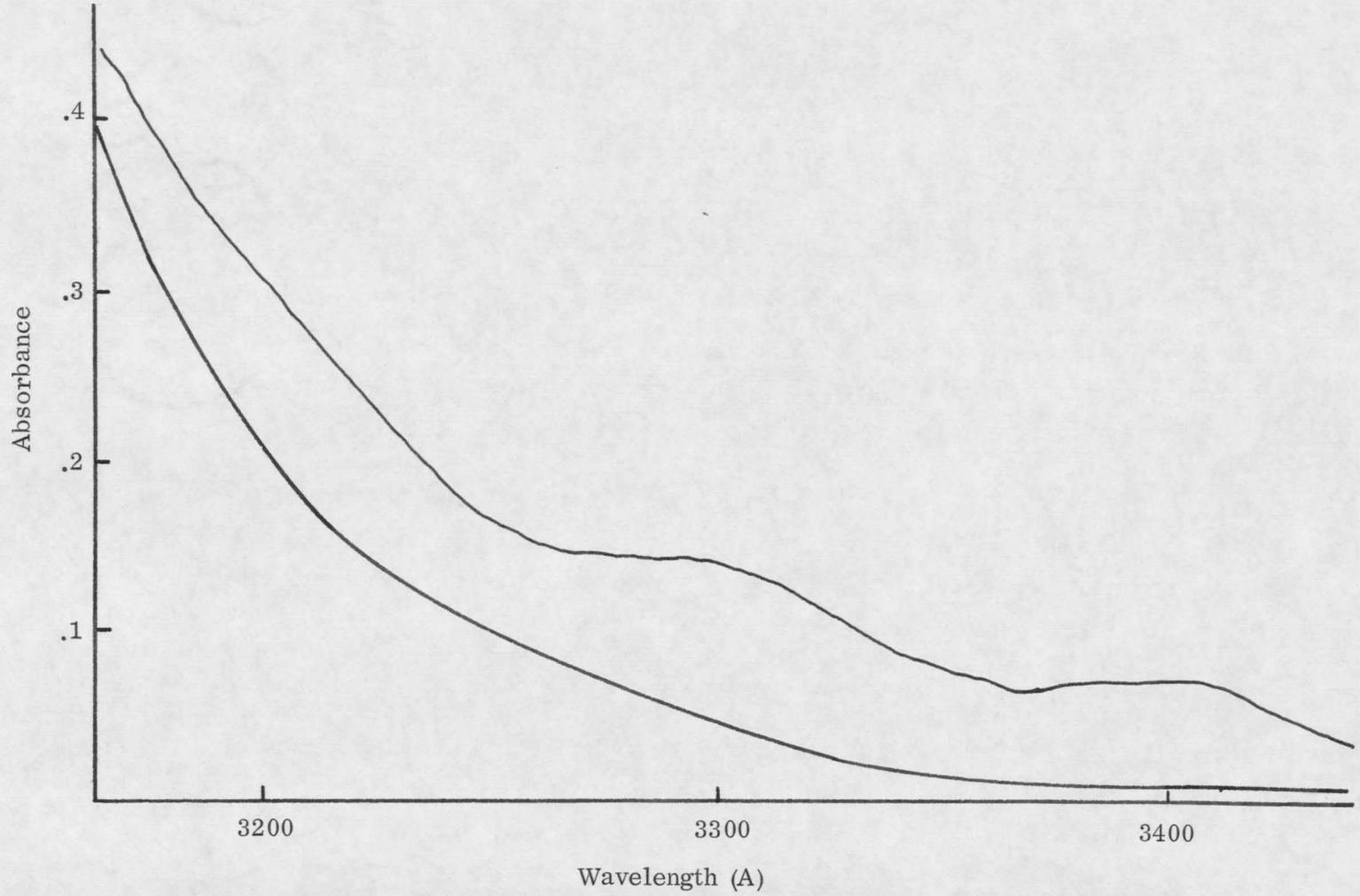
Spectrum No. 6. 3.25 molal arsenic trichloride in naphthalene, air reference, 10 cm cells.



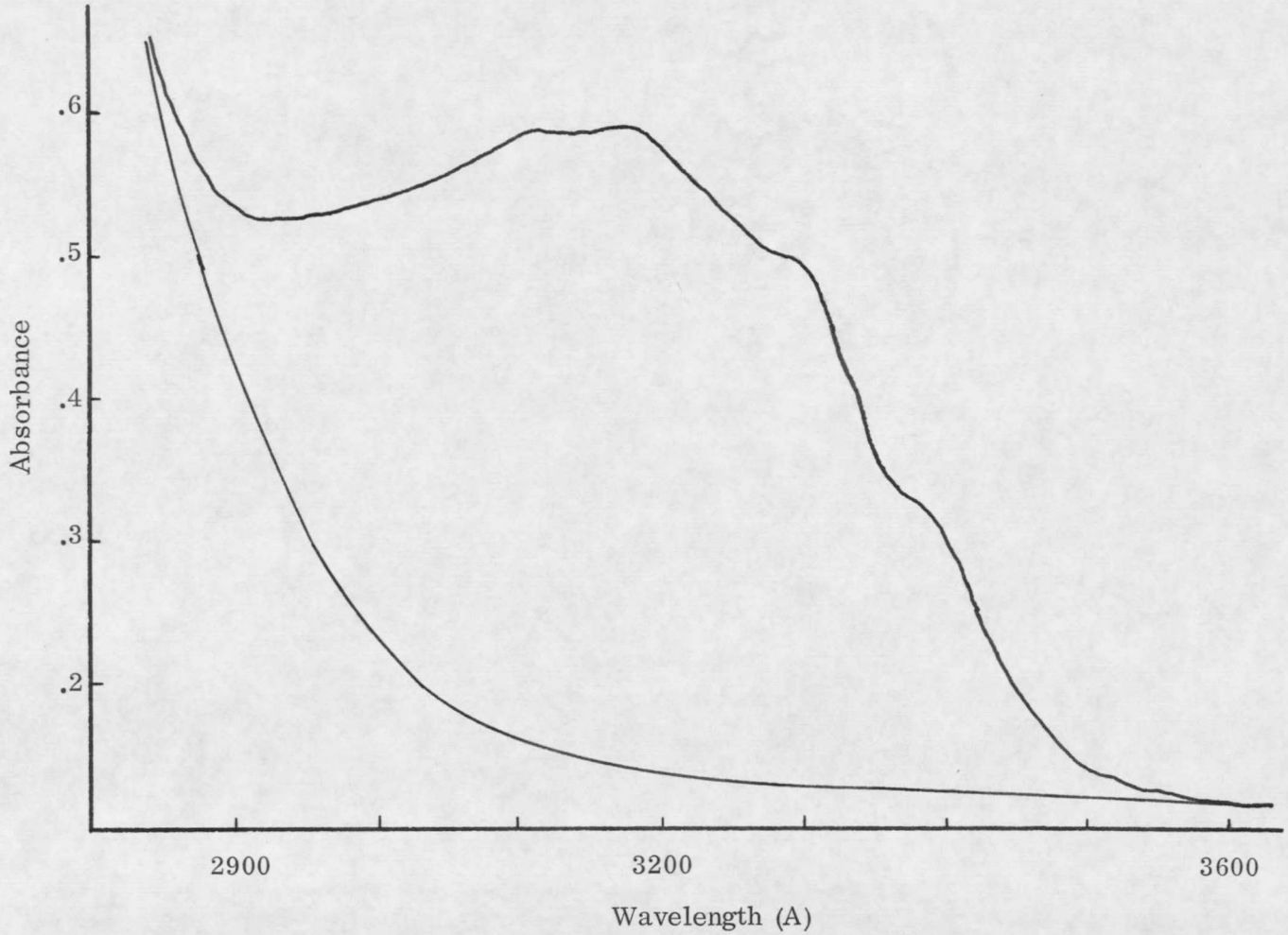
Spectrum No. 7. 0.010 molal bismuth trichloride in naphthalene, 5 cm cells, naphthalene reference.



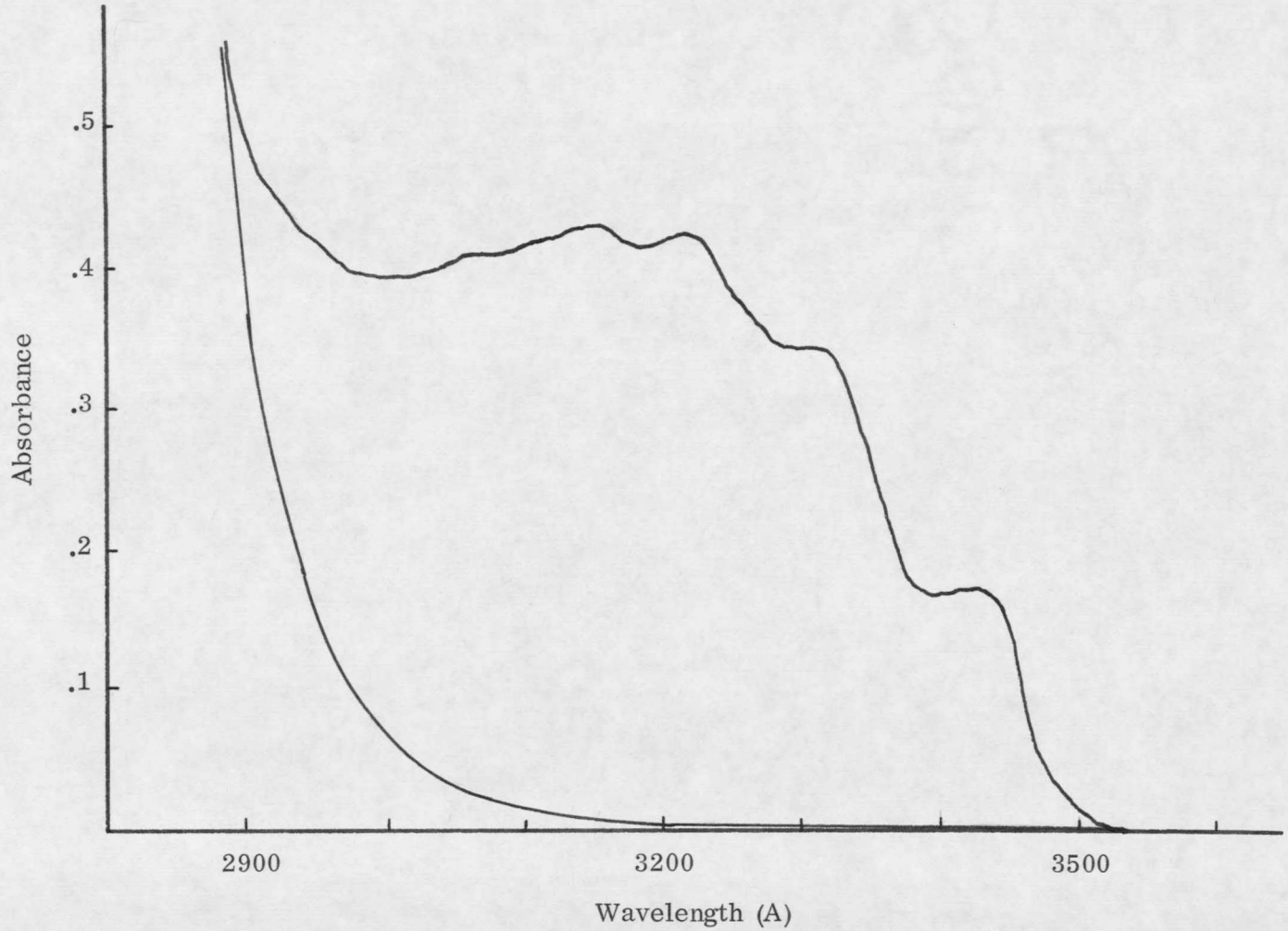
Spectrum No. 8. 2.77×10^{-3} molal stannic chloride in naphthalene, 10 cm cells, air reference.



Spectrum No. 9. 0.02 molar mercuric chloride in benzene, 10 cm cells.



Spectrum No. 10. 0.10 molar phenylmercuric acetate in glacial acetic acid, 10 cm cells.



Spectrum No. 11. 0.05 molar diphenylmercury in chloroform, 10 cm cells.

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