cis and *trans* configurations for this 22-electron molecule.

An interesting result of the N_2O_2 calculation is the geometry of the $N_2O_2^{4-}$ ion. This would be isoelectronic with Cl_2O_2, another loose dimer, recently detected by matrix-isolation techniques by Pimentel and coworkers.[32] The calculations suggest that the $N_2O_2^{4-}$ ion should be bent, but with completely free rotation about the central bond.

Conclusion

A combination of semiquantitative calculations and qualitative molecular orbital reasoning can provide simple pictorial explanations for the shapes of polyatomic molecules. Where symmetry helps out, one can also get an understanding of isomerization processes. Many other interesting series of related molecules remain to be studied in a similar way.

Acknowledgment. I gratefully acknowledge the generous amount of computer time made available by the Computer Center of the University of South Carolina.

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The Interaction of Oxygen with Organic Molecules. I. Absorption Spectra Caused by Adsorbed Organic Molecules and Oxygen

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Abstract: Electronic absorption spectra, arising from interactions between oxygen and aromatic compounds adsorbed on porous glass or silica gel, were measured. Unlike the spectra induced by oxygen in organic solvents, absorption spectra with a certain number of clear maxima have been observed in most cases. These maxima have been interpreted to represent separate charge-transfer excited states, of which the theoretical aspects are discussed. The effect on the spectra of lowering the temperature has been studied. Strong adsorption spectra caused by the singlet → triplet transitions have been obtained for naphthalene adsorbed on porous glass immersed in liquid oxygen. Charge-transfer absorption spectra arising from the interaction between iodine and aniline derivatives adsorbed on silica gel have also been measured, and the results are discussed in relation to the oxygen–aniline systems.

Evans found that oxygen dissolved in aromatic solvents gives rise to extra absorption bands at wavelengths longer than the absorption edges of the aromatics.[1a] Many experiments related to this problem have been done, and now it seems to be quite reasonable that the extra absorption bands are caused by the charge-transfer interaction between oxygen, as an electron acceptor, and organic molecules, as electron donors, although no stable complexes are formed between them.[1c,2–5] Therefore, these absorption bands can be considered to be quite similar to the contact charge-transfer bands found in iodine solutions.[6,7] Evans[1b] also found additional small peaks at the long-wavelength tail of the extra absorption bands when oxygen is dissolved under high pressure in the solutions of aromatic compounds, or when it is mixed with aromatic vapor. He concluded that these weak bands are singlet–triplet absorption bands enhanced by oxygen. Theoretical investigations of these phenomena were also undertaken by many authors.[3,8,9] The contribution of the charge-transfer state in which an electron is removed from the donor molecule to the oxygen molecule has been pointed out. However, the relative importance of the charge-transfer or the exchange mechanism in perturbing the singlet–triplet transition is still open to question, though it would depend on the system, as well as on the orientation of one molecule to another. No detailed information on the electronic energy levels of the charge-transfer states has been obtained, since the extra absorption bands found so far in solutions show no absorption maxima but increase monotonically toward shorter wavelength.

It was expected that the technique of adsorption would afford new means for understanding the nature of intermolecular interaction.[10–12] In the present work, the measurement and interpretation of the absorption spectra caused by the interaction between oxygen and organic molecules adsorbed on the solid surface are carried out. Moreover, the characteristics of intermolecular interaction in the adsorbed state, as well

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(1) (a) D. F. Evans, *J. Chem. Soc.*, 345 (1953); (b) *ibid.*, 1351, 3885 (1957); 2753 (1959); 1735 (1960); (c) *ibid.*, 1987 (1961).

(2) A. U. Munck and J. R. Scott, *Nature*, 177, 587 (1956).

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(12) N. Okuda, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **82**, 1118 (1961).

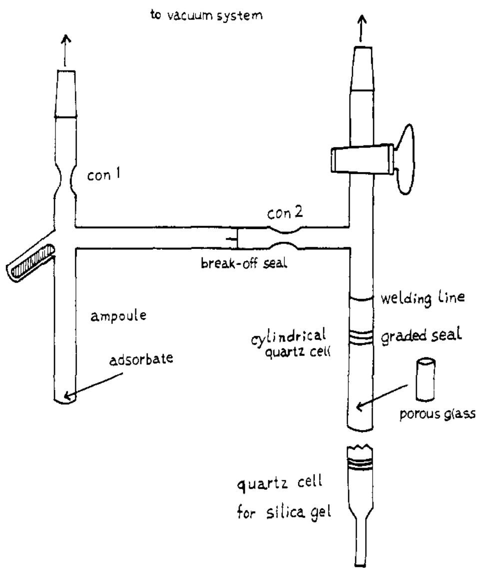

Figure 1. Adsorption apparatus.

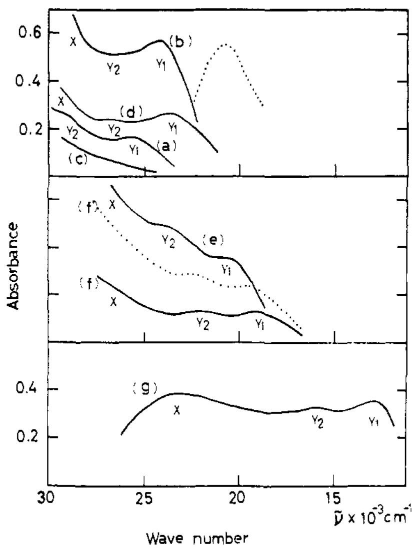

Figure 2. Electronic absorption spectra caused by oxygen and aromatic amines adsorbed on porous glass. The glass was exposed to an oxygen atmosphere of 200 mm at room temperature: (a) N-methylaniline, (b) N,N-dimethylaniline, (c) N,N-dimethyl-*o*-toluidine, (d) N,N-dimethyl-*m*-toluidine, (e) N,N-dimethyl-*p*-toluidine, (f) N,N-diethylaniline, (f′) the same as (f), cooled to 77°K, (g) N,N-dimethyl-*p*-phenylenediamine, (h) fluorescence spectrum for N,N-dimethylaniline.

as the extra absorption spectra obtained so far in solutions, are discussed.

Experimental Section

Materials. The commercial high-purity oxygen was led into a vacuum line and purified by several distillations using liquid nitrogen as a coolant, and the vapor of liquid oxygen at liquid nitrogen temperature was used. The silica gel used was from Nakarai Chemical Corp. (30-42 mesh). Porous glass was donated by Central Research Laboratory of Mitsubishi Electric Corp., Amagasaki, Japan. The glass was supplied in the form of a tube with an outer diameter of 11 mm, from which many short tubes were cut for use. The surface area was measured to be about 271 m^2/g. It is transparent up to near-ultraviolet region.

N-Methylaniline, N,N-diethylaniline, N,N-dimethylaniline, and its *o*-, *m*-, and *p*-methyl derivatives were obtained commercially, dried with sodium hydroxide, and distilled under reduced pressure. Commerically available N,N-dimethyl-*p*-phenylenediamine was purified by distillation followed by sublimation in vacuum. N,N,-N′,N′-Tetramethyl-*p*-phenylenediamine was purified in the same way as described elsewhere.[13] Naphthalene was purified by column chromatography over silica gel, followed by recrystallization. Iodine was purified by sublimation in vacuum.

Procedure. The adsorbent, porous glass or silica gel, was heated in the air at 500° for about 20 hr. Then it was placed in the quartz cell, which is welded onto the apparatus as shown in Figure 1. After evacuation and heating the adsorbent at 500° for 6–8 hr in the cell, the apparatus was sealed off at the constriction (con 1) and removed from the vacuum line at the conical joint. The adsorbent was then exposed to the vapor of organic material, which was previously degassed in the ampoule, *via* a breakoff seal, at room temperature. The vapor which was not adsorbed in the system was taken back into the ampoule cooled by liquid nitrogen, after which the ampoule was sealed off at con 2.

Absorption spectra were measured before and after the introduction of oxygen into the cell. The absorption spectra of the porous glass adsorbates were measured with a Cary Model 15 spectrophotometer, with the measuring light passing through the cell and sample. For the case of silica gel, a quartz cell having two planar windows separated from each other by 2 mm was used. The absorption spectra of the silica gel adsorbates were measured by the reflection method with a Shimadzu Multi-Purpose recording spectrophotometer, Model 50L. The monochromatized sample beam of the spectrophotometer hits upon the planar surface of the quartz cell, which is placed just before the photomultiplier. The specularly reflected light is led into a specially designed absorber, and only the intensity of the randomly reflected light is measured by the photomultiplier. That the scanning of the ratio of the light intensity to the intensity of the reference beam agrees fairly well with the absorption spectra measured by usual methods is well established for powder materials, adsorbed species, opaque materials, etc.

The emission spectra were measured with an Aminco-Bowman spectrophotofluorimeter, using powdered porous glass put in an apparatus similar to that shown in Figure 1, with the quartz cell having a diameter of only 4 mm. The decay of the emission was followed by use of a high-speed flash apparatus constructed by N. Mataga and others.

Results

Absorption Spectra Caused by Oxygen. The absorption spectra caused by oxygen and aromatic amines adsorbed on the porous glass are shown in Figure 2, where the absorption before introducing oxygen is subtracted. The intensity of the absorption bands increased with the pressure of oxygen introduced, and gradually decreased with evacuation. When the sample was cooled down to liquid nitrogen temperature, the intensity of the absorption bands increased as shown in Figure 2 in the case of N,N-diethylaniline, and the bands showed a slight blue shift. The change of the spectra with temperature was found to be reversible. We could also obtain almost the same absorption spectra in the case of oxygen and aromatic amines adsorbed on silica gel, as shown in Figure 3, where the ordinate, "reflex attenuance," corresponds to absorbance. It is attributable to the reflection method that the intensity of the absorption bands of silica gel adsorbates is weak in the shorter wavelength region, as compared with that of porous glass adsorbates. This was confirmed by measuring the well-known absorption spectrum of Würster's blue iodide adsorbed on silica gel, by both reflection and transmission methods with the Multi-Purpose spectrophotometer.

Distinct absorption maxima and shoulders were found for adsorbed oxygen and aromatic amines except for N,N-dimethyl-*o*-toluidine. Each of the absorption spectra seems to consist of a strong band, hereafter

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[13] N. Yamamoto, Y. Nakato, and H. Tsubomura, *Bull. Chem. Soc. Jap.*, 39, 2903 (1966).

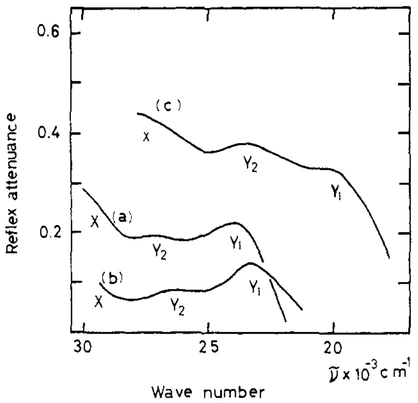

Figure 3. Electronic absorption spectra caused by oxygen and N,-N-dimethylaniline derivatives adsorbed on silica gel. The silica gel was exposed to an oxygen atmosphere of 200 mm at room temperature: (a) N,N-dimethylaniline, (b) N,N-dimethyl-*m*-toluidine, (c) N,N-dimethyl-*p*-toluidine.

called X band, in the shorter wavelength region, and two weak bands, Y_1 and Y_2, in the longer wavelength region. The maximum of the X band is found clearly only in the case of N,N-dimethyl-*p*-phenylenediamine (DMPD). In other cases the whole shape of the X band cannot be observed, because it overlaps with the strong absorption band of the organic molecule itself.

In the case of DMPD, which has an ionization potential lower than the alkyl derivatives of anilines, the specimen giving the absorption spectrum shown in Figure 2 was found to be unstable. Under humid conditions, for example, when the sample was exposed to air, $DMPD^+$ [14] formed rapidly. In the case of N,N,-N′,N′-tetramethyl-*p*-phenylenediamine (TMPD), which has an ionization potential lower than DMPD, $TMPD^+$ [13] formed instantaneously on introducing oxygen at 200 mm pressure, possibly because of very slight moisture contained in the oxygen, and by virtue of the effect of the polar adsorbent. The absorption spectrum caused by oxygen could not be detected on account of the strong absorption of $TMPD^+$ formed.

We also tried to measure emission spectra of the porous glass adsorbates, by exciting them at the absorption bands caused by oxygen and aromatic amines. Although no emission was detected at room temperature, broad and weak emission bands were detected distinctly in the cases of N,N-dimethylaniline, N,N-dimethyl-*m*-toluidine, N,N-dimethyl-*p*-toluidine, and N-methylaniline, at liquid nitrogen temperature. These emission bands form approximate mirror images of the Y_1 bands, which are the extra absorption bands at the longest wavelengths. As an example, the emission spectrum for the case of N,N-dimethylaniline is shown in Figure 2. The decay of this emission was found to be exponential, the lifetime being 110 nanosec.

Absorption Spectra Caused by Liquid Oxygen. In order to see the effect of liquid oxygen on the spectra of adsorbates, we have carried out some experiments. A piece of porous glass was placed in an apparatus such as shown in Figure 1. Naphthalene was adsorbed on it, and the cell was cooled with liquid nitrogen. Then, dry oxygen was introduced into the cell until the porous glass was immersed in liquid oxygen. The absorption spectra caused by liquid oxygen and by an oxygen atmosphere of 200 mm are shown in Figure 4. As Figure 4 shows, a pronounced shoulder was present at *ca.* 26 kK for the spectrum obtained in the latter case, while in the former case, there is no such shoulder at the same region. It was confirmed that the weak absorption bands observed in liquid oxygen at the long wavelength tail agree very well with the singlet–triplet absorption bands of naphthalene, measured with oxygen dissolved in the solutions under high pressure.[1b,15] The molar extinction coefficient of the singlet–triplet absorption band at the longest wavelength was calculated to be 0.4, based on the content of naphthalene in the glass. The same experiment was done also for N,N-dimethylaniline. The sample turned a deep yellow in liquid oxygen. The absorption spectrum is much stronger than that shown by the curve of Figure 2(b), and rises monotonically toward shorter wavelength. However, the absorption spectrum obtained after the removal of liquid oxygen from the glass was the same as that shown in Figure 2.

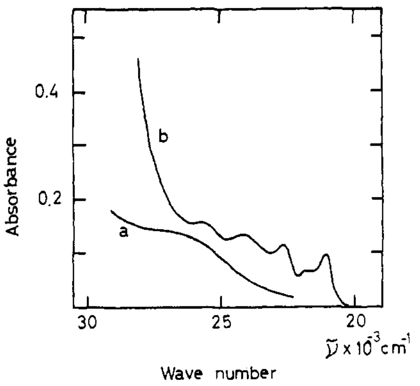

Figure 4. Electronic absorption spectra caused by oxygen and naphthalene adsorbed on porous glass: (a) in an oxygen atmosphere of 200 mm at room temperature, (b) in liquid oxygen at liquid nitrogen temperature.

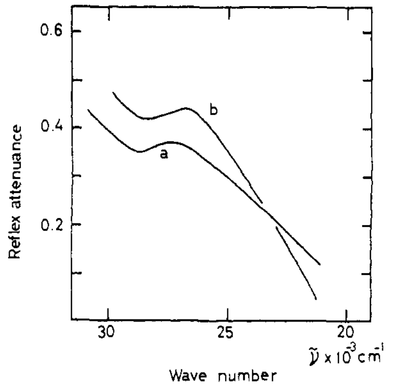

Figure 5. Electronic absorption spectra caused by iodine and N,N-dimethylaniline derivatives adsorbed on silica gel. The silica gel was exposed to iodine vapor at room temperature: (a) N,N-dimethylaniline, (b) N,N-dimethyl-*p*-toluidine.

Absorption Spectra Caused by Iodine. We also tried to measure absorption spectra by exposing the silica gel adsorbates of aniline derivatives to iodine vapor instead of oxygen. The absorption spectra caused are shown in Figure 5. Studies on the molecular complexes

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[14] K. Kimura, K. Yoshinaga, and H. Tsubomura, *J. Phys. Chem.*, 71, 4485 (1967).

[15] G. J. Hoijtink, *Mol. Phys.*, 5, 643 (1962).

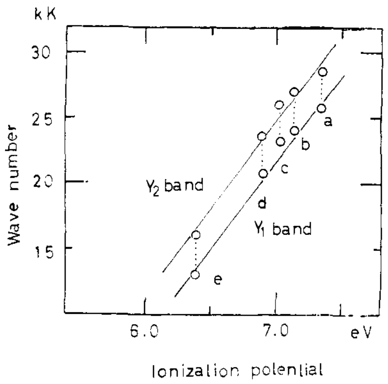

Figure 6. Relationship between the wave numbers of the Y_1 and Y_2 bands and the ionization potentials of organic molecules: (a) N-methylaniline, (b) N,N-dimethylaniline, (c) N,N-dimethyl-*m*-toluidine, (d) N,N-dimethyl-*p*-toluidine, (e) N,N-dimethyl-*p*-phenylenediamine.

of various anilines with iodine, in solution, have been previously made by Chandra and Mukherjee,[16] and by Tsubomura.[17] Chandra and Mukherjee have observed a characteristic charge-transfer absorption band in the near-ultraviolet region as well as another charge-transfer band present in the shorter wavelength region. The absorption spectra obtained on silica gel in this laboratory agree closely with those reported,[16] although they show a slight red shift and have more distinct absorption bands in the near-ultraviolet region.

Discussion

As described in the Experimental Section, the intensities of the extra absorption bands of several organic molecules adsorbed on the solid surfaces together with oxygen decrease with evacuation and increase reversibly with temperature decrease. This indicates that the observed bands are due to weak interactions between organic molecules and oxygen, and not to the oxidation products. This result also shows that the interaction between oxygen and organic molecules is strengthened at lower temperature. This increased interaction may be due to the closer contact between the adsorbed organic molecules and oxygen at low temperature.[18]

It has been confirmed from studies of solutions that the smaller the ionization potential of the organic molecule, the longer the wavelength of the spectra caused by oxygen.[3] It may also be found from Table I that the smaller the ionization potential, the smaller the wave numbers of the Y_1 and Y_2 bands. Moreover, Figure 6 shows two parallel linear relationships between wave numbers and ionization potentials (see also Table I). It seems, therefore, very reasonable to postulate that the absorption bands caused by oxygen and aromatic amines adsorbed on a solid surface are also due to transitions to charge-transfer states, with oxygen as an electron acceptor and an organic molecule as an electron donor. In the case of N,N-dimethyl-*o*-toluidine, the absorption maximum and shoulder are not found distinctly in the longer wavelength region, and the intensity of the absorption band is very weak. This result may be explained by the steric effect of the *o*-methyl group, which prohibits the approach of the lone-pair electrons of the nitrogen atom, because of the twisting of the dimethylamino group.[17,19] In the case of DMPD and TMPD, having ionization potentials lower than alkyl derivatives of anilines, the complexes with oxygen were found to be very unstable and to form cation radicals of the donors easily. This finding seems to indicate that these complexes have an appreciable ionic character, even in the ground state, because of the stronger charge-transfer interaction between oxygen and donors.

Table I. The Wave Numbers of the Y_1 and Y_2 Bands and the Ionization Potentials of Organic Molecules

Organic molecule	Y_1 band, ν_1, kK	Y_2 band, ν_2, kK	$\Delta E = \nu_2 - \nu_1$, kK	Ionization potential, eV
N-Methylaniline	25.6	(28.6)[a]	(3.0)	7.35[c]
N,N-Dimethylaniline	24.2	27.1	2.9	7.14[c]
N,N-Dimethyl-*o*-toluidine[b]				
N,N-Dimethyl-*m*-toluidine	23.8	26.7	2.9	(7.0)[d]
N,N-Dimethyl-*p*-toluidine	20.5	23.6	3.1	(6.9)[d]
N,N-Diethylaniline	19.2	22.1	2.9	
N,N-Dimethyl-*p*-phenylenediamine	13.0	16.0	3.0	(6.4)[d]
N,N,N′,N′-Tetramethyl-*p*-phenylenediamine				6.25[e]

[a] A weak shoulder. [b] No distinct band maximum has been obtained. [c] F. I. Vilesov, *Zh. Fiz. Khim.*, **35**, 2010 (1961). [d] These values were tentatively estimated from the ionization potentials of aniline, *p*-toluidine, *p*-phenylenediamine (G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **63**, 6 (1959)), and N,N-dimethylaniline (ref *c* given above). [e] M. Batley, Ph.D. Thesis, University of Sydney, 1966.

It is worth noting that the separation between the Y_1 and Y_2 bands is roughly constant, irrespective of the donor molecules, as shown in Table I. This strongly suggests that each of the two bands (Y_1 and Y_2) corresponds to the transition of an electron from the highest filled orbital of the organic molecule to each of the two electron-accepting orbitals of oxygen which is occupied by an unpaired electron. A simple theoretical treatment will be made later in this paper, based on this assumption.

In the case of DMPD, the separation between the Y_1 band and the X band is found to be 10.3 kK. This can be compared with the separation between the two charge-transfer bands found for the TMPD–TCNE (tetracyanoethylene) complex, 13.0 kK.[20] It is generally accepted that the two charge-transfer bands observed in the TCNE complexes with some aromatic molecules are due to the transition of an electron from, respectively, the highest occupied and the second highest occupied orbital of the donor to the lowest vacant orbital of TCNE.[21,22] Taking account of the difference between TMPD and DMPD, our results on the Y_1 and X bands may be interpreted as arising from the transitions from the highest and the second highest occupied levels of DMPD.

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(16) A. K. Chandra and D. C. Mukherjee, *Trans. Faraday Soc.*, **60**, 62 (1964).

(17) H. Tsubomura, *J. Am. Chem. Soc.*, **82**, 40 (1960).

(18) H. Tsubomura and R. P. Lang, *J. Chem. Phys.*, **36**, 2155 (1962).

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(20) W. Liptay, G. Briegleb, and K. Schindler, *Z. Elektrochem.*, **66**, 331 (1962).

(21) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(22) T. Matsuo and H. Aiga, *Bull. Chem. Soc. Jap.*, **41**, 271 (1968).

It is also well known that benzene derivatives having strong electron-donating substituents show two distinct charge-transfer bands in their complexes with iodine, such as N,N-dimethylaniline–I_2[16] or anisole–I_2,[23] and these are attributed to the two donor orbitals[24] such as were described in the case of TMPD–TCNE complex. The absorption spectra found for substituted anilines and iodine adsorbed on silica gel show distinct maxima, as seen in Figure 5. The maximum and the stronger absorption in the shorter wavelength region are interpreted to be caused, respectively, by the transition from the highest and the second highest filled orbital of the donor. Similarly, the absorption spectra due to oxygen and aniline derivatives adsorbed on porous glass seem to have Y_1 and Y_2 bands and stronger absorption in the shorter wavelength region. The latter may be interpreted to be the X band, arising from the charge transfer from the second highest occupied orbitals of the donor molecules.

The emission spectra found for the adsorbed oxygen–aromatics form approximate mirror images with the Y_1 bands, as stated in the Results of this paper. This indicates that these emission bands are most probably the charge-transfer fluorescence, *i.e.*, due to the transition from the lowest charge-transfer state (corresponding to the Y_1 band) to the ground state. If this interpretation is true, these bands are the first example of charge-transfer fluorescence involving oxygen as the electron acceptor. The lifetime measured, 110 nanosec, is rather long compared with other charge-transfer fluorescence previously measured. This result is consistent with the theoretical interpretation, in that the transition for the present case is geometrically nearly forbidden.

Simple Theoretical Investigation of the Absorption Spectra Caused by Oxygen. Let us discuss the validity of the assignment for the Y_1 and Y_2 bands described in the preceding section. Although a donor molecule might interact with many surrounding oxygen molecules simultaneously, we assume for simplicity that the oxygen and donor moleule form a 1:1 pair. The appearance of the definite peaks in each of the absorption spectra of the oxygen–aromatic systems strongly indicates the formation of complexes having fairly strong binding and rather fixed geometries. This statement is in contrast to our previous opinion that there is no complex formed between oxygen and organic molecules in solutions.[3] It seems highly probable that in the adsorbed state, the attractive force between adsorbent and adsorbate may cause the oxygen and aromatic molecules to bind each other at a fixed configuration or fixed configurations.

The energy of the charge-transfer states E_{ct} may generally be approximated by the equation

$$E_{ct} = I_D - E_A - Q \qquad (1)$$

where I_D and E_A are, respectively, the ionization potential of the donor and the electron affinity of the acceptor, in this case, oxygen. Q is the electrostatic interaction energy between D^+ and A^-. According to our theory, the Y_1 and Y_2 bands correspond to the charge-transfer transition from the highest occupied MO, Ψ_D, of the donor to the two lowest vacant MO's of an oxygen molecule, Ψ_x and Ψ_y. These can be given as follows by the use of real 2pπ atomic wave functions, π_x and π_y for one oxygen atom and π_x' and π_y' for another oxygen atom.

$$\begin{aligned} \psi_x &= 2^{-1/2}(\pi_x - \pi_x') \\ \psi_y &= 2^{-1/2}(\pi_y - \pi_y') \end{aligned} \qquad (2)$$

In eq 2, π_x and π_y are directed, respectively, along the x and y axes, both perpendicular to the molecular axis. For simplicity, the overlap integrals between π_x and π_x' and π_y and π_y' are neglected.

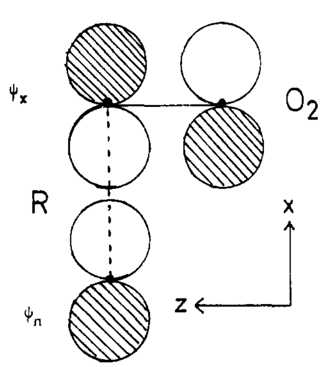

Figure 7. Schematic diagram indicating a particular arrangement for the donor orbital ψ_n and the oxygen acceptor orbital ψ_x. Shaded and unshaded volumes in the orbitals indicate positive and negative regions, respectively.

The separation between bands Y_1 and Y_2 should then correspond to the difference between the energies of the two charge-transfer states E_{ctx} and E_{cty} as given by eq 1. In the present case, both I_D and E_A for the Y_1 and Y_2 bands may be taken as equal, and, therefore, neglecting exchange or other minor interactions, the energy difference between Y_1 and Y_2 may be set equal to the difference between the electrostatic energy Q for the two charge-transfer states.

To calculate the electrostatic energy, the wave function for the highest filled MO of the donor and the shape of the D···A pair must be known. For the methyl-substituted anilines, it has been pointed out that the nitrogen 2pπ AO plays an overwhelmingly large part in the highest filled MO.[17] Hence, for a simple treatment, the highest filled MO of these molecules may be approximated simply by the 2pπ AO of nitrogen. Taking into account the theoretical result that the nitrogen 2pπ AO, ψ_n, plays the largest part in the charge transfer, it may be reasonable to assume that the structure of the complex is such that the axis of ψ_n is perpendicular to the molecular axis of oxygen. Tentatively, the structure is assumed to be as shown in Figure 7, where ψ_n lies in an end-on position with the oxygen π_x AO. This assumption of the structure is still very artificial in the choice of the position of the nitrogen atom with respect to that of oxygen, but a minor change in that will not produce a large difference in the results.

The electrostatic energy has been calculated as intermolecular two-center Coulomb integrals[25] by use of the multipole expansion method proposed by Parr.[26] Figure 8 shows the energy difference ΔE between E_{cty} and E_{ctx} plotted *vs.* the distance between the oxygen and nitrogen atoms. At a distance of 3 Å, a reasonable value for

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(23) P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1189 (1957).
(24) L. E. Orgel, *ibid.*, **23**, 1352 (1955).
(25) K. Kimura and H. Tsubomura, *Mol. Phys.*, **11**, 349 (1966).
(26) R. G. Paar, *J. Chem. Phys.*, **33**, 1184 (1960).

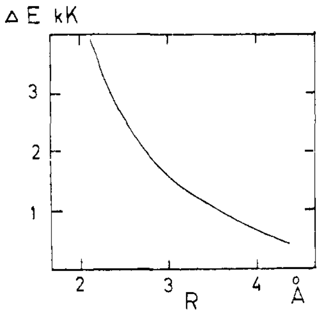

Figure 8. The energy difference ΔE calculated as a function of the distance R between oxygen and nitrogen atoms.

the nitrogen–oxygen distance in complexes, ΔE becomes 1.5 kK, with $E_{\mathrm{ct}y}$ higher than $E_{\mathrm{ct}x}$. This is approximately half of the observed separation between the Y_1 and Y_2 bands, which is about 3 kK in most cases (Table I). Taking into account the neglect of exchange interactions between donor and acceptor orbitals which seems to contribute to the separation between $E_{\mathrm{ct}y}$ and $E_{\mathrm{ct}x}$, and the interaction of the charge-transfer states with various other excited states, the agreement between experimental and observed values may be taken to be fairly good. It can also be concluded from these calculations that the Y_1 band and the fluorescence band mentioned before correspond to CT_x, and the Y_2 band, weaker than the former, to CT_y.

Further Discussion on the Absorption Spectra of N,N-Dimethylaniline and Naphthalene Caused by Oxygen. Evans measured the absorption spectrum caused by bubbling oxygen into pure N,N-dimethylaniline and found a shoulder near 380 mμ, which he regarded as one of the two charge-transfer bands corresponding to the two ionization potentials predicted for substituted benzenes.[1c] Recently, this result of Evans has been reconfirmed in this laboratory for the *n*-hexane solution of N,N-dimethylaniline.

It seems most likely that the above-mentioned shoulder corresponds to our Y_1 and Y_2 bands amalgamated together, though the Y_1 band lies at longer wavelength than the shoulder. The difference between the absorption spectrum obtained for the adsorbate and that obtained in solution may be caused by the change of environment. In the adsorbed state, we can expect the more restricted orientation and closer contact between anilines and oxygen, the red shift being attributable to the effect of the electric field of the polar adsorbent, while in solution an oxygen molecule is considered to interact weakly with surrounding organic molecules having random orientations. Similar explanation can be given for the complexes with iodine.

Dijkgraaf, *et al.*,[27] found a pronounced shoulder near 350 mμ (29 kK) in addition to the singlet–triplet absorption bands of naphthalene, when oxygen under high pressure was dissolved in the chloroform solution of naphthalene, and assigned it to a simultaneous transition involving naphthalene and oxygen.[8] This result has recently been confirmed in this laboratory. However, in the present results for liquid oxygen (Figure 4(b)), the shoulder is apparently missing, while the curve for gaseous oxygen (Figure 4a) has a distinct shoulder at about 27 kK.

It has already been seen that the shoulder appearing for N,N-dimethylaniline–oxygen in solution (26 kK) is split to Y_1 (24 kK) and Y_2 (27 kK) bands when adsorbed on porous glass or silica gel. Therefore, it is rather likely that the shoulder reported by Dijkgraaf, *et al.*, may be due to a transition essentially identical with that for the shoulder found here for the adsorbed specimens. If this interpretation is true, the shoulder is due more probably to a charge-transfer-type transition than to the simultaneous transition, although the two relevant excited states may mix together to a certain extent. The reason that no strong shoulder is found in the case of liquid oxygen (Figure 4b) is not clear at present.

In closing, it may be suggested that further study on the interaction between adsorbed molecules and oxygen would provide valuable information on the nature of the interaction between these molecules, which may be important in connection with biological problems, for example, those related to hemoglobin or cytochrome.

Acknowledgment. The authors wish to express their thanks to Professor S. Teranishi for his suggestions on the use of porous glass, and to Professor N. Mataga and H. Ohari for helping us to measure the decay of emission spectra.

(27) C. Dijkgraaf, R. Sitters, and G. J. Hoijtink, *Mol. Phys.*, **5**, 643 (1962).