[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, UNIVERSITY OF CHICAGO]

The Spectra of Iodine Solutions. III. The ${}^3\Pi_1$-${}^1\Sigma^+$ Transition of the Iodine Molecule in Solution[1]

BY JOE HAM[2]

RECEIVED FEBRUARY 2, 1954

The absorption of the ${}^3\Pi_1 - {}^1\Sigma^+$ transition of the iodine molecule is found in heptane solution near 690 mμ and its oscillator strength is estimated to be $f = 2.9 \times 10^{-4}$. The upper state of this transition arises from the same electronic configuration as the upper state of the much stronger visible ${}^3\Pi_0{}^+ - {}^1\Sigma^+$ absorption and of the ${}^1\Pi - {}^1\Sigma^+$ which is hidden by the visible absorption. The intensity of this infrared transition is larger than by previous estimates and it lies at shorter wave lengths. The present more accurate values remove some difficulties encountered by Mulliken in a previous theoretical discussion, and they support one of two alternative assignments in the I_2 and Br_2 visible spectra given by him. At low temperatures in the ether–iodine complex, both the ${}^3\Pi_0{}^+ - {}^1\Sigma^+$ and the ${}^2\Pi_1 - {}^1\Sigma^+$ transition peaks are shifted toward shorter wave lengths by about 4000 kayser.

Introduction

The visible absorption of the iodine molecule arises from transitions between the ${}^1\Sigma^+$ ground state and the excited states ${}^3\Pi_0{}^+$ and ${}^1\Pi$,[3] the transition ${}^3{}_0\Pi^+ - {}^1\Sigma^+$ being much the more intense.[3a] (Although the notation for Λ-S coupling is employed here, the large amount of spin-orbit coupling in the iodine atoms modifies considerably the properties of these wave functions.) The transition to the ${}^1\Pi$ state is not directly observed, but its presence follows necessarily from theoretical considerations. It must be buried under the much stronger ${}^3\Pi_0{}^+ - {}^1\Sigma$ transition. From the same electronic configuration as these excited states, there is a ${}^3\Pi_1$ state which gives rise to weak absorption bands and continuum in the vapor phase in the near infrared.[4]

Solution Spectrum at Room Temperature.—Measurements of the spectrum of iodine in *n*-heptane solution disclosed a shoulder on the side of the visible absorption near 690 mμ when log ε was plotted against the wave length (Fig. 1). This absorption is almost certainly the ${}^3\Pi_1 - {}^1\Sigma^+$ absorption, since it is near the position of the analyzed vapor bands and, on the basis of convincing theoretical considerations, no other transitions should occur in this spectral region. By subtracting graphically the absorption due to the stronger visible transitions, the intensity of this transition could be estimated. Its oscillator strength appeared to be approximately $f = 2.9 \times 10^{-4}$, which may be compared with the previously estimated value, $f = 4.5 \times 10^{-5}$, based upon the appearance pressure of the vapor absorption.[3,4] Although the errors introduced by subtracting the visible absorption are likely to be quite large, the solution value is definitely much more reliable than that taken from the appearance pressure data. The latter could easily differ from the actual intensity by a factor of two or three, but the observed factor of six seems very large. It is possible, however, that the process of solution may have modified the intensity of this weak transition.

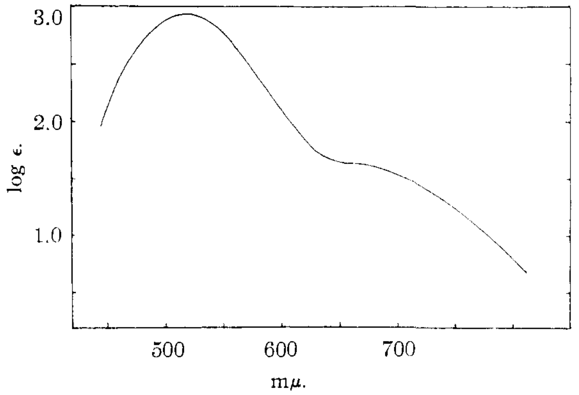

Fig. 1.—Logarithm of the molar extinction coefficient of iodine in *n*-heptane *vs.* frequency. The weak band near 690 mμ is the ${}^3\Pi_1 - {}^1\Sigma^+$ transition, while the strong band is the ${}^3\Pi_0{}^+ - {}^1\Sigma^+$ transition (plus to some extent, the weaker ${}^1\Pi - {}^1\Sigma^+$ transition) of the iodine molecule.

Brown[4] estimated the maximum of this weak absorption, which lies in the continuum, to be at 13,660 ± 90 kayser[5] in the vapor phase, whereas in the present work it was estimated to be at 14,600 ± 300 kayser in solution. This difference may conceivably be a solvent effect or possibly it may be due to the high temperatures used in the previous work which might cause a shift in the maximum.

Theoretical Discussion—In the Λ-S coupling approximation, the wave functions for the ${}^3\Pi_1$ and ${}^1\Pi$ states differ principally in their spin factors. The introduction of spin-orbit coupling mixes these wave functions with each other so that the ${}^3\Pi_1 - {}^1\Sigma^+$ transition acquires some intensity from the ${}^1\Pi - {}^1\Sigma^+$ transition. The amount of mixing is given by a parameter which may be estimated from the spin-orbit coupling parameter of the iodine atom and the singlet–triplet splitting for the molecule. The latter may be obtained by an extrapolation from the lighter halogens. Unfortunately, there are two alternative assignments of the Br_2 visible spectrum. The visible absorption of Br_2 consists of two peaks; the stronger one at shorter wave lengths is certainly the ${}^1\Pi - {}^1\Sigma^+$, but the one at longer wave lengths, which appears as a shoulder on the side of the stronger absorption, may be either (1) ${}^3\Pi_0{}^+ - {}^1\Sigma^+$ or (2) ${}^3\Pi_1 - {}^1\Sigma^+$.[3a] These two assignments yield two different estimates for

---

(1) This work was assisted in part by the Office of Ordnance Research under Project TB2-0001 (505) of Contract DA-11-022-ORD-1002 with The University of Chicago.

(2) Atomic Energy Commission predoctoral fellow, 1951–1953. Jackson Laboratory, E. I. du Pont de Nemours and Co., Wilmington, Del.

(3) (a) R. S. Mulliken, *Phys. Rev.*, **57**, 500 (1940); (b) P. Venkateswarlu, *ibid.*, **81**, 821 (1951), gives a recent summary of the iodine molecular spectra literature.

(4) W. G. Brown, *ibid.*, **38**, 1187 (1931).

(5) Kayser (formerly cm.$^{-1}$). See "Transactions of the Joint Commission for Spectroscopy," *J. Opt. Soc. Am.*, **43**, 410 (1953).

the mixing parameter in I_2. Using the present revised data on the infrared absorption, these two values predict the strength of the hidden $^1\Pi - {}^1\Sigma^+$ transition in I_2 to have a strength of either (1) $f = 1.1 \times 10^{-3}$ or (2) $f = 4.3 \times 10^{-4}$. This corresponds to either 8 or 3% of the intensity of the visible absorption.

The two alternative coupling parameters also give two estimates of the $^3\Pi_0{}^+$, $^3\Pi_1$ separation. These are (1) 3860 kayser and (2) 4660 kayser and the maximum separation for the extreme case of complete spin-orbit coupling is 5067 kayser.[3a] These values are all much smaller than the interval 5540 kayser for the observed separation using Brown's data. The present investigation, however, indicates that the observed interval is 4600 ± 300 kayser, at least in heptane solution.

Independent of the amount of singlet–triplet mixing, calculations indicate that the sum of the strengths of the $^1\Pi - {}^1\Sigma^+$ and $^3\Pi_1 - {}^1\Sigma^+$ transitions probably should be somewhat larger in iodine than in the lighter halogens.[6] Using the two estimates of the strength of the $^1\Pi - {}^1\Sigma^+$ transition given in the preceding paragraph, two different estimates of the total strength are obtained. Only assignment (1) gives a total intensity that is larger than the observed intensity for the same quantity in Cl_2. Mulliken considered assignment (1) the most likely one at the time of his paper, even though there were several difficulties.[3a] Most of these difficulties are eliminated by using the frequency and intensity for the infrared band found in the present study, so that assignment (1) for the Br_2 and I_2 visible spectra is probably correct.

In additional effect of using the present frequency and intensity of the infrared band is to predict a position of the $^1\Pi - {}^1\Sigma^+$ that is in the banded region of the $^3\Pi_0{}^+ - {}^1\Sigma^+$ visible absorption. Since the $^1\Pi$ state has a repulsive potential curve going to the atoms in their ground states, absorption to this state should result in dissociation.

A complete explanation of the strong intensity of the $^3\Pi_0{}^+ - {}^1\Sigma^+$ visible band of iodine may yet alter the above discussion. This transition is forbidden under the coupling assumptions used to derive the above singlet–triplet mixing. Two possible mechanisms have been proposed for its strong intensity but neither is very satisfactory.[3a] One of these involves the mixing of the upper state of the $^1\Sigma^+ - {}^1\Sigma^+$ (N, V), which appears near 190 mμ, into the $^3\Pi_0{}^+$ state. Measurements of the $^1\Sigma^+ - {}^1\Sigma^+$ intensity in solution show that this intensity is much smaller[7] than previously supposed; therefore, a much greater mixing of the $^1\Sigma^+$ with the $^3\Pi_0{}^+$ would be required to explain the observed intensity than is reasonable.[3a]

Behavior of the $^3\Pi_1$-$^1\Sigma^+$ Transition in Complexes at Low Temperatures.—A study of the weak $^3\Pi_1 - {}^1\Sigma^+$ absorption in complexes was made in an effort to ascertain if shifts occurred for this absorption similar to those which occur in the visible absorption peak upon complexing. Unfortunately, for most complexing solvents at room temperature, a considerable fraction of the iodine present is uncomplexed. The absorption of the uncomplexed iodine masks any shoulder or peak corresponding to a shifted $^3\Pi_1 - {}^1\Sigma^+$ transition in the spectrum of complexed iodine.

At low temperatures, however, nearly all of the iodine is complexed in some solutions[8] so that there is no absorption of free iodine to obscure the position of this weak band. Figure 2 shows a portion of the spectrum of iodine in a hydrocarbon glass containing 5 volume per cent. of diethyl ether. The visible iodine band is shifted from 520 mμ at room temperature to 433 mμ for the ether complex at low temperatures.[8] At low temperatures, there appears an absorption near 530 mμ of about the same intensity (ϵ_{max} 25) as the $^3\Pi_1 - {}^1\Sigma^+$ observed near 690 mμ for free iodine at room temperature. This may reasonably be identified as the same absorption shifted in the complex at low temperature. It is doubtful that this absorption could be due to the presence of uncomplexed iodine since it is at slightly longer wave lengths than the absorption of uncomplexed iodine at room temperatures and since the equilibrium constant is probably immense at low temperatures. Although ΔH is not known for the ether–iodine complex, it should be −2 kcal./mole or less (the dioxane–iodine complex has $\Delta H = -3.5$ kcal./mole[9]). When this is combined with the equilibrium constant at room temperature,[10] an estimate of the equilibrium constant at liquid nitrogen temperatures is about 10^5, so that less than 0.02% of the iodine would be uncomplexed if the solutions reached equilibrium.

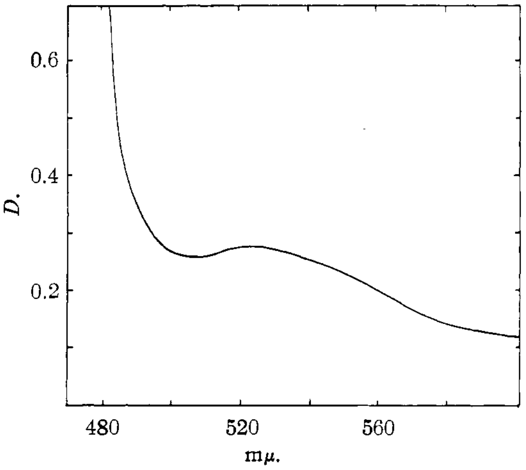

Fig. 2.—Optical density of a solution of iodine in a glass containing ether at low temperatures.

If this interpretation is adopted, the frequency shifts of the $^3\Pi_0{}^+ - {}^1\Sigma^+$ and $^3\Pi_1 - {}^1\Sigma^+$ bands of iodine are 3900 and 4300 kayser, respectively, in going from uncomplexed iodine at room temperature to iodine in the ether complex at low temperatures.

I wish to express my gratitude to Prof. R. S. Mulliken who suggested the search for the $^3\Pi_1 - {}^1\Sigma^+$ band and who pointed out the theoretical implications.

Wilmington, Delaware

---

(6) R. S. Mulliken, *J. Chem. Phys.*, **8**, 234 (1940).

(7) J. S. Ham, J. R. Platt and H. McConnell, *ibid.*, **19**, 1301 (1951).

(8) J. S. Ham, This Journal, **76**, 3881 (1954).

(9) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

(10) J. S. Ham, *J. Chem. Phys.*, **20**, 1170 (1952).