would be expected to contribute to the electronic structure of the protonated *cis* isomer, giving the ground state a reduction in bond order at the central double bond compared to the neutral species.

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Far-Infrared Intensity Studies of Iodine Complexes

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Abstract: Measurements have been made of the frequencies and intensities of the "I–I stretching" vibrations for I_2 complexes with pyridine, 3-picoline, 2,6-lutidine, benzene, *p*-dioxane, and diethyl sulfide, and more qualitative measurements on the I_2 complexes with acetonitrile and diethylamine. The measurements were made using polyethylene cells, with a Beckman IR-11 far-infrared spectrometer. For the first three complexes, comparison can be made to the results obtained by Lake and Thompson, using an interferometer. The agreement is good enough to verify the general reliability of these techniques. The results are interpreted in terms of the theory given by Friedrich and Person. For the amine·I_2 complexes, the results are quite reasonable. The results for dioxane·I_2 and for diethyl sulfide·I_2 appear to be anomalous.

A number of spectroscopic studies have been made of charge-transfer complexes with iodine as the acceptor. These studies have been extensively reviewed by Briegleb,[3a] by Andrews and Keefer,[3b] and by Mulliken and Person.[4] Because of instrumental problems, relatively few studies have been made before this year in the far-infrared region where the ν(I–I) vibrational band would be expected.[5] Studies in the far-infrared region have been made for other halogen molecules acting as acceptors, and some ν(X–X) or ν(X–Y) band intensity estimates have been obtained.[6–8] Qualitative studies of the low-frequency infrared spectra of the pyridine·I_2[9–11] and benzene·I_2[9] complexes have been reported and recently, while our manuscript was being prepared, absolute intensity measurements of the I–I and of the N–I stretching vibrations have been presented for iodine complexes with pyridines.[12]

Intensity values for the I–I stretch in I_2 complexes provide a test of the recent theoretical expression[13] for the transition moment and relative change in force constant, $\Delta k/k$. Furthermore, there has been some question about the accuracy of far-infrared intensity work, so that it seems worthwhile to report our results for comparison with those already published.[12]

We have therefore attempted to measure the frequency and intensity of ν(I–I) for D–I_2 complexes with as many different donor molecules as possible. For the most part we have been able to study only *n* donors,[14] and chemical problems (with further reactions) or spectral problems (with interference) have limited even those. However, we have managed to extend our studies to a few systems not included by Lake and Thompson,[12] with some rather puzzling results.

Experimental Section

(a) **Chemicals.** Mallinckrodt analytical reagent grade iodine (resublimed) was used without further purification.

Phillips Petroleum Co. commercial grade *n*-heptane was shaken for 12-hr periods with concentrated sulfuric acid until the acid ceased to turn yellow. It was then washed thoroughly with sodium carbonate solution and water and dried by passing through a 10-ft column packed with silica gel. Final drying was achieved by standing for several days over (Linde) molecular sieves. Purity checks were made by comparison with the known absorption[15] in the 200–250-mμ region.

Dioxane (from Matheson Coleman and Bell) was refluxed with hydrochloric acid for about 8 hr, cooled, and treated with potassium hydroxide (solid) until all the water had been removed.[16] The dioxane was allowed to stand over molecular sieves for a day, and it was then refluxed over sodium in a nitrogen atmosphere for 6 hr and fractionated from sodium, bp 100° (lit.[16] 101°). The ultraviolet absorption spectrum showed only very weak impurity bands. The dioxane was stored in a dark bottle but was used as soon after purification as possible.

The benzene, pyridine, and acetonitrile were Eastman Spectrograde solvents. They were used without further purification as were the 2,6-lutidine and diethylamine (Eastman), and the 3-picoline (Matheson). All the materials were, however, thoroughly dried over molecular sieves immediately prior to use.

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[13] H. B. Friedrich and W. B. Person, *J. Chem. Phys.*, **44**, 2161 (1966).

[14] R. S. Mulliken, *J. Chim. Phys.*, 20 (1964).

[15] "Spectroquality Solvents—Spectra, Physical Properties, Specifications, and Typical Uses," Matheson Co., Norwood, Ohio, 1965.

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Table I. Equilibrium Constants and $\Delta H°$ Values for Some I_2 Complexes

Complex (solvent)	Literature: K_c (t, °C), l./mole	Literature: $-\Delta H°$, kcal/mole	Value chosen: K_c (35°), l./mole	Value chosen: $-\Delta H°$, kcal/mole
Pyridine $\cdot I_2$[a] (n-heptane)	135 ± 20 (25)	7.8	88[b] (*cf.* 62)[c]	7.8
3-Picoline $\cdot I_2$[d] (n-hexane, lit.; n-heptane, here)	223 (25)		145[b] (*cf.* 149)[c]	7.8[e]
2,6-Lutidine $\cdot I_2$[f] (CCl_4, lit.; n-heptane, here)	51 (25)		33[b] (*cf.* 41)[c]	7.8[e]
Benzene $\cdot I_2$[g] (CCl_4, lit.; pure benzene)	0.15 (25)	1.3	0.14	1.3
Diethyl sulfide $\cdot I_2$[h] (n-heptane)	180 (25)	8.0 ± 0.3	119[b]	8.0
p-Dioxane $\cdot I_2$[i] (CCl_4, lit.; n-heptane here)	0.89 (36)	3.4	0.89	3.4
Acetonitrile $\cdot I_2$[j] (CCl_4)	0.42 (25)	2.2	0.36	2.2
Diethylamine $\cdot I_2$[k] (n-heptane)	4260 (30)	9.7	4260 (30°)	9.7

[a] From H. D. Bist and W. B. Person, *J. Phys. Chem.*, **71**, 2750 (1967). This value is selected as appropriate for pyridine $\cdot I_2$ in n-heptane after consideration of results by C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, **76**, 3869 (1954); A. I. Popov and R. H. Rygg, *ibid.*, **79**, 4622 (1957); J. N. Chaudhuri and S. Basu, *Trans. Faraday Soc.*, **55**, 898 (1959); and A. G. Maki and E. K. Plyler, *J. Phys. Chem.*, **66**, 766 (1962), as well as the new experimental results by Bist and Person. [b] Calculated from K_c at 25° with the $\Delta H°$ listed here. [c] Computed from the K given by Lake and Thompson,[12] using the ΔH value listed here. [d] From G. Aloisi, G. Cauzzo, G. Giacometti, and U. Mazzucata, *Trans. Faraday Soc.*, **61**, 1406 (1965). [e] Assumed to be the same as for the pyridine $\cdot I_2$ complex. [f] From Popov and Rygg, footnote *a;* see also Chaudhuri and Basu, footnote *a*. [g] From a summary by Briegleb, ref 4a. [h] H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961); M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962). [i] From J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. Chim.*, **71**, 1104 (1952). [j] From W. B. Person, W. C. Golton, and A. I. Popov, *J. Am. Chem. Soc.*, **85**, 891 (1963). [k] From H. Yada, J. Tanaka, and S. Nakakura, *Bull. Chem. Soc. Japan*, **33**, 1660 (1960).

(b) Cells and Instruments Used. The liquid cells were constructed from high-density polyethylene sheets described in detail elsewhere.[17] Spacers and gaskets were cut from polyethylene and "Teflon" sheets. Typical path lengths for measurements on the I_2 complexes varied from 2.0 to 7.0 mm. Path lengths were measured with a micrometer. As a further check on the path length, the known intensity of the band in liquid benzene at about 300 cm^{-1} was used.[17]

A Beckman IR-11 spectrometer was used in the double-beam mode. This machine was calibrated using the atmospheric water and carbon dioxide lines found between 50 and 700 cm^{-1}.[18] For further discussion of this instrument, see ref 17. However, according to our tests, the false energy near 200 cm^{-1} was less than 1%.

(c) Preparation of Sample Solutions. Stock solutions of iodine and of the donor were made up in the appropriate freshly dried solvent (usually n-heptane). Complex solutions were then prepared by pipetting known amounts of donor and acceptor solutions into a small, stoppered flask and mixing well. The concentration of complex in solution was calculated from the equilibrium formation constant K_c (at the "beam" temperature of about 34°) for the particular system under investigation. A summary of K_c and $\Delta H°$ data for the complexes studied is given in Table I. The initial concentrations were not corrected for the slight change expected due to the temperature change from 25 to 34°.

All intensity measurements were made within 2 hr of mixing the donor and iodine solutions. This reduced the possibility of error due to polyhalide ion formation. Also the cell was refilled after each single band had been run in order to reduce the possibility of error due to complex decomposition while in contact with the metal cell parts.

The I_0 curve was obtained in the usual way using an appropriately diluted sample of the donor alone. In most cases I_0 and I matched up well in the wings of the band (see Figure 1).

In general, our experimental procedure was similar to that of Lake and Thompson.[12] However, their measurements were made using an interferometer while ours were made with a Beckman IR-11. We changed the path lengths of our cells as needed, while they used a fixed path-length cell of 9.35 mm (which was longer than ours). We calibrated the path length of our polyethylene cells using the intensity of the benzene band at 300 cm^{-1} which we had previously measured in a cell with CsI windows. Hence, we had to assume that any warping of the cells was the same for both the n-heptane solutions and the benzene liquid; also the accuracy of the path length measurement then depends upon the accuracy of the intensity measurement of our standard.[17] Finally, we have always used higher concentrations of pyridine (by about a factor

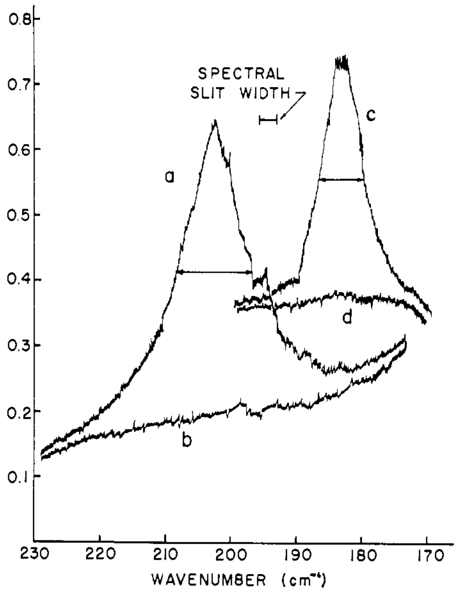

Figure 1. Typical spectral traces of the I–I stretching vibration in different complexes. (a) Benzene $\cdot I_2$ complex in n-heptane: path length 5.66 mm; concentration of complex 0.155 *M;* ν_{max} 205 cm^{-1}, $\Delta\nu_{1/2}$ 7.5 cm^{-1}. (b) Background for (a): cell + benzene. (c) Pyridine $\cdot I_2$ complex in n-heptane: path length 2.33 mm; concentration of complex 0.014 *M;* ν_{max} 183 cm^{-1}, $\Delta\nu_{1/2}$ 7.0 cm^{-1}. (d) Background for (c): cell + n-heptane + pyridine.

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Table II. Intensity Results for the ν(I–I) Band in Various I_2 Complexes

Complex	ν_{max}, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	Run no.	*l*, mm	*nl* × 10^6, mole cm^{-2}	*Bnl* (av) area, cm^{-1}	B_i, cm mmole^{-1} (darks)
Pyridine·I_2[a]	183	6.5	1	2.33 ± 0.02	1.57 ± 0.02	3.2 ± 0.2	2050 ± 140
			2	2.33 ± 0.02	1.93 ± 0.02	3.9 ± 0.3	1960 ± 150
			3	3.33 ± 0.03	2.25 ± 0.02	5.0 ± 0.5	2230 ± 230
			4	3.33 ± 0.03	3.52 ± 0.02	7.9 ± 0.6	2250 ± 170
			5	2.33 ± 0.02	2.46 ± 0.03	5.8 ± 0.4	2340 ± 200
			6	2.33 ± 0.02	3.04 ± 0.03	6.9 ± 0.4	2280 ± 130
3-Picoline·I_2[a]	182	6.5	1	3.33 ± 0.03	2.33 ± 0.02	5.2 ± 0.4	2230 ± 190
			2	4.66 ± 0.04	3.26 ± 0.03	6.3 ± 0.7	1940 ± 230
			3	2.33 ± 0.02	2.57 ± 0.02	5.8 ± 0.3	2250 ± 150
			4	3.33 ± 0.03	3.68 ± 0.02	8.6 ± 0.3	2330 ± 100
			5	2.33 ± 0.02	3.19 ± 0.02	7.5 ± 0.3	2360 ± 100
2,6-Lutidine·I_2[a]	184	7.0	1	3.33 ± 0.03	1.80 ± 0.02	3.6 ± 0.2	2020 ± 110
			2	2.33 ± 0.02	1.26 ± 0.02	2.9 ± 0.7	2310 ± 110
			3	2.33 ± 0.02	1.88 ± 0.02	4.5 ± 0.2	2420 ± 110
			4	3.33 ± 0.03	2.61 ± 0.02	5.3 ± 0.7	2030 ± 190
			5	2.33 ± 0.02	2.00 ± 0.02	5.1 ± 0.5	2550 ± 180
			6	3.33 ± 0.03	2.86 ± 0.02	6.3 ± 0.6	2220 ± 210
			7	1.84 ± 0.08	1.40 ± 0.06	4.1 ± 0.9	2960 ± 700
			8	1.84 ± 0.08	1.51 ± 0.06	4.1 ± 0.3	2690 ± 320
Benzene·I_2[b]	205	12.0	1	4.68 ± 0.04	74.1 ± 0.6	12.4 ± 1.2	170 ± 15
			2	4.68 ± 0.04	49.2 ± 0.4	7.9 ± 0.3	160 ± 10
			3	4.68 ± 0.04	59.3 ± 0.5	9.4 ± 0.5	160 ± 10
			4	4.68 ± 0.04	65.6 ± 0.5	10.5 ± 0.5	160 ± 10
			5	5.66 ± 0.05	79.3 ± 0.7	12.1 ± 0.4	150 ± 10
			6	5.66 ± 0.05	87.9 ± 0.7	13.9 ± 0.3	160 ± 3
			7	4.68 ± 0.04	72.7 ± 0.6	11.7 ± 0.4	160 ± 10
Diethyl sulfide·I_2[a]	172	7.5	1	4.66 ± 0.04	6.71 ± 0.05	10.4 ± 0.6	1550 ± 100
			2	4.66 ± 0.04	6.77 ± 0.06	10.3 ± 0.3	1520 + 60
			3	2.33 ± 0.02	3.38 ± 0.03	4.8 ± 0.2	1410 ± 80
			4	4.66 ± 0.04	5.23 ± 0.04	8.1 ± 0.2	1540 ± 60
			5	2.33 ± 0.02	2.61 ± 0.03	3.7 ± 0.1	1410 ± 60
			6	3.36 ± 0.02	4.00 ± 0.06	5.5 ± 0.2	1390 ± 60
			7	3.36 ± 0.02	5.13 ± 0.04	6.8 ± 0.3	1330 ± 70
Dioxane·I_2[a]	206	6.0	1	4.64 ± 0.05	4.13 ± 0.04	2.5 ± 0.3	600 ± 80
			2	4.64 ± 0.05	4.95 ± 0.05	3.0 ± 0.2	610 ± 40
			3	5.70 ± 0.10	6.07 ± 0.10	4.7 ± 0.5	770 ± 70
			4	5.70 ± 0.10	5.31 ± 0.09	3.9 ± 0.5	740 ± 110
			5	6.97 ± 0.07	7.69 ± 0.08	5.6 ± 0.5	730 ± 80

[a] In *n*-heptane solution. [b] In pure benzene.

of 10) in our studies than were used by Lake and Thompson,[12] partly because we needed higher concentrations of complex with our shorter cells. We do not know whether or not the concentration of pyridine in our cells (less than 0.1 *M*) was high enough to change the nature of the solvent enough to account for the differences between our measurements and those of Lake and Thompson.[12]

Results

Typical spectra of ν(I–I) are shown in Figure 1. For each particular complex concentration or path length, the absorption band was scanned four times so that any change with time in the apparent integrated intensity, B_i, could be detected and so that the areas could be averaged. Areas were measured directly from the spectrum with a planimeter since they were recorded as linear absorbance plotted against linear wavenumber.

The results are given in Table II along with random errors estimated from the scatter of measured variables affecting the apparent intensities. The *Bnl* values for each of the bands in Table II were plotted according to Beer's law. Typical plots are shown in Figure 2, illustrating graphically the scatter of data. Table III summarizes the final intensity results. The random error here was obtained from the Beer's law plots by drawing lines of maximum and minimum slope through the data points as indicated in Figure 2. The "best" straight line to give B_i in Table III was drawn with a visual averaging of data. A more detailed treatment of these data is not justified by their accuracy.

Table III. Summary of ν(I–I) Band Intensities for I_2 Complexes

Complex	ν_{max},[a] cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	B_i, cm/mmole	B_i,[b] cm/mmole
Pyridine·I_2	183	6.5	2190 ± 250	2930
3-Picoline·I_2	182	6.5	2220 ± 270	2760
2,6-Lutidine·I_2	184	7.0	2260 ± 300	2980
Benzene·I_2	205	12.0	160 ± 20	
Diethyl sulfide·I_2	172	7.5	1450 ± 150	
p-Dioxane·I_2	206	6.0	680 ± 100	
Diethylamine·I_2	172	8.0	>700	

[a] Random error is ±1 cm^{-1}. [b] From Lake and Thompson.[12]

The principal sources of systematic error involved in making intensity measurements on complex solutions have been outlined elsewhere.[17] One important possible random error for these complexes is in the value for the concentration of the complex, due to the uncertainties in the values of K_c. It should also be mentioned that errors caused by finite resolution of the instrument are likely to be more important than for the ICl complexes[17] because of the relatively small band width of ν(I–I). In no case, however, was the slit width more than one-third of the observed band width, so that this error is expected to be less than those due to other effects.

In addition to the complexes shown in Table II, attempts were made to study the iodine complexes with acetonitrile and diethylamine. Study of the former is complicated because acetonitrile does not dissolve in nonpolar hydrocarbon solvents such as *n*-heptane. It does dissolve in carbon tetrachloride which has, however, even at medium path lengths, a fairly strong band at 218 cm^{-1}. The ν(I–I) band in this complex may be seen in CCl_4 solution at about 205 cm^{-1}, but it is very weak and no reasonable estimate of its intensity could be obtained since it is overlapped by the 218-cm^{-1} CCl_4 band.

The diethylamine·I_2 complex has a very large K_c value (Table I). However, it appears to react further so that it was difficult to keep the complex in solution in *n*-heptane. On mixing the two components, a brown solution is formed which shows an absorption band at 172 cm^{-1} due to ν(I–I) and also a weak broad band at 140 cm^{-1} (not present in pure amine solutions) which could possibly be the ν(N–I) band but is probably due to a small amount of I_3^- reaction product. However, these absorption bands rapidly disappear with time, and a solid precipitate appears in the cell. The dark brown solid is fairly readily soluble in water, indicating that it is ionic (possibly $Et_2NHI^+ \cdot I_3^-$). It would appear that the *solution* does contain a 1 : 1 complex for a short period. The intensity of ν(I–I) in this complex was estimated roughly to be at least 700 cm/mmole, assuming that only a 1 : 1 complex is formed in solution. This estimate is a minimum value since some solid may already have precipitated before the spectrum was obtained.

Discussion

One of the most important results of this study, perhaps, is the comparison in Table III between our intensity results for the complexes of I_2 with the pyridine derivatives and those found for the same complexes by Lake and Thompson.[12] One of the real questions regarding experiments in the far-infrared region of the spectrum has been whether or not it is actually possible to measure meaningful intensities there. We believe the agreement in Table III between our results and those of Lake and Thompson is good enough so that we may be reassured on this question. The self-consistency of both sets of results is high enough so that we might expect better agreement. However, the differences for the three complexes between these two sets of results are less than three times the scatter in our data, so that the agreement is probably about as good as can be expected.

The fact that our results for these amine complexes all cluster about a value of 2200 cm/mmole, while Lake and Thompson's results cluster about a value of 2900 cm/mmole, does suggest that a systematic error may account for the difference. The source of this error might be that different values of equilibrium constants were used to calculate the concentration of the complexes. However, the values which were measured and used by Lake and Thompson at 18° can be corrected for the change in temperature and compared with the corresponding values which we used at 35°. The comparison in Table I shows that the two sets of equilibrium constants are practically identical. For example, the use of Lake and Thompson's value of K_c for the pyridine·I_2 complex to compute the concentration of complex and thus the intensity changes our B_i value only to 2460 cm/mmole. The changes for the other two complexes would be even less.

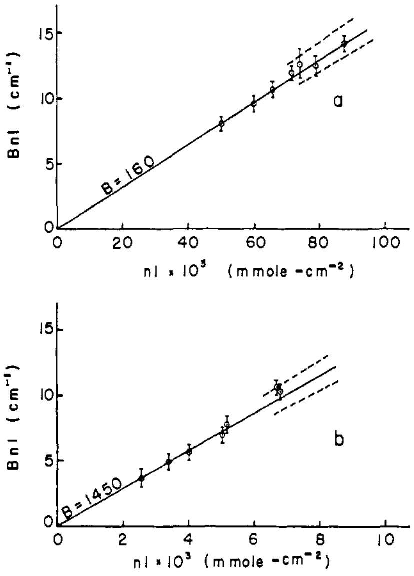

Figure 2. Typical Beer's law plots for the ν(I–I) band: (a) benzene·I_2 complex, ν(I–I) 205 cm^{-1}; (b) diethyl sulfide·I_2 complex, ν(I–I) 172 cm^{-1}.

Hence, the most likely explanation for a systematic difference between Lake and Thompson's results and ours is the fundamental difference in technique between the use of an interferometer and of a grating spectrometer. The most obvious difference is the way in which I_0 (the donor–solvent background) is obtained, since a small constant error here could easily lead to an error of 10–15% in the intensity, B_i. At any rate, the discrepancy between the two sets of results is not unreasonable.

Now let us consider further the results in Table III. We see there that the inactive ν(I–I) mode in free I_2 becomes active when iodine is complexed with an electron donor. The frequency is shifted toward lower frequencies from the "free-I_2" value of 213 cm^{-1} in the vapor or 207 cm^{-1} from the Raman spectrum of I_2 in CCl_4,[19] and the intensity increases from 0 to as much as 3000 cm/mmole. Only a few iodine complexes have previously been studied in this region of the spectrum, but it has been shown[6-8,13] that this behavior is characteristic of the ν(X–Y) band for complexes of $a\sigma$ acceptors, X–Y, such as Br_2, ICl, and ICN complexes.

The interpretation of these spectral changes upon formation of a charge-transfer complex was first formulated by Ferguson and Matsen.[20] As the halogen (X–Y) bond in the complexed halogen stretches, the vertical electron affinity ($E_A{}^v$) of the electron acceptor changes and the contribution of the dative structure

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Table IV. Summary of $\Delta k/k$ and ϵ_a Values for Complexes with I_2

Complex	ν_{max},[a] cm^{-1}	Intensity, B_i for ν(I–I), cm/mmole	"Diatomic molecule approx," ϵ_a[c]	k for complexed I_2, mdyn $Å^{-1}$	"Diatomic molecule approx," $\Delta k/k$[d]
Benzene·I_2	205	160 ± 20	1.5 ± 0.2	1.57	0.02
Pyridine·I_2	183	2190 ± 250	5.6 ± 0.8	1.25	0.22
3-Picoline·I_2	182	2220 ± 270	5.7 ± 0.8	1.24	0.23
2,6-Lutidine·I_2	184	2260 ± 300	5.8 ± 0.8	1.27	0.21
Diethyl sulfide·I_2	172	1450 ± 150	4.7 ± 0.5	1.11	0.31
p-Dioxane·I_2	205	700 ± 100	3.2 ± 0.5	1.57	0.02
Acetonitrile·I_2	205	...	...	1.57	0.02
Diethylamine·I_2	172	>700[b]	>3.2[b]	1.11	0.31

[a] Frequency in complex; all solutions in *n*-heptane except the benzene·I_2 complex, which was in pure benzene, and acetonitrile·I_2 complex, which was in carbon tetrachloride. The error is ±1 cm^{-1} in all cases. [b] Estimated minimum value only (see text). [c] Calculated from $\epsilon_a = 0.01537\sqrt{B_i/0.01576}$ of ref 7. [d] Calculated assuming $k_{I-I}^0 = 1.60$ mdyn/Å (or ν_0 207 cm^{-1}) (see text). Better values can be estimated if the system is treated like a triatomic molecule D···I–I. See text and ref 13 and 22.

to the ground-state wave function of the complex changes. Because of this "electron vibration" or "vibronic interaction",[13] a large dipole moment change occurs for the ν(X–Y) vibration so that its absorption intensity increases considerably when such interaction occurs. This mechanism[20] predicts a regular increase in the intensity of ν(X–Y) as the donor–acceptor strength increases. Furthermore, we may expect that the frequency of ν(X–Y) would decrease as the strength of the interaction increases, since the frequency shift (or rather the relative change in force constant $\Delta k/k$) is taken to be a measure of b, the coefficient of the dative structure.[6–8, 13] In fact, we assume simply that[21]

$$\Delta k/k \simeq b^2 + abS_{01} \qquad (1)$$

rather than using the more complicated relationship suggested previously.[13] When the added effective charge, $\epsilon_a (\equiv \partial\mu/\partial r)$, was plotted against $\Delta k/k$, the relative change in force constant for the X–Y bond, computed assuming the complexed halogen molecule to be a slightly perturbed diatomic molecule, then a rather good straight line was found empirically. Person and Friedrich have concluded, however, that the empirical straight-line relationship between ϵ_a and $\Delta k/k$ is probably fortuitous.[13]

Table IV shows the values $\Delta k/k$ (computed from the "diatomic molecule approximation") and ϵ_a for the I_2 complexes which we have studied. These points do not lie on the line found previously for the complexes,[8] or even on a different straight line of their own. Thus, even though ν(I–I) lies at approximately the same frequency in both the dioxane and benzene complexes, the intensities differ by a factor of 4. Similarly, ν(I–I) in the diethyl sulfide complex lies 10 cm^{-1} below its position in the aromatic amine complexes, but its intensity for the $Et_2S \cdot I_2$ complex is considerably *less* than that in pyridine·I_2, for example.

In the interpretation of results from IBr complexes,[22] it was suggested that the normal coordinate describing ν(I–I) is expected to mix, in strong complexes, with the donor–halogen stretching vibration, ν(D–I). Hence, the change in force constant of the I–I bond is not simply related to the frequency shift, and the "diatomic molecule approximation" breaks down. In the spectra of more stable n·σ complexes of ICl and IBr,[10, 11, 17, 22] a band at lower frequencies than ν(X–Y) is observed which can be assigned to the N–I vibration. In the aromatic amine·ICl complexes, ν(N–I) is approximately one-third as intense as ν(I–Cl)[17] (in benzene solution). This corresponding ν(N–I) vibration in the aromatic amine·I_2 complexes has been observed by Lake and Thompson[12] (at 94 cm^{-1} for pyridine·I_2). Our own results do not extend in general to such low frequencies, but qualitative survey spectra confirm their report. This ν(N–I) band is so close to ν(I–I) at 183 cm^{-1} that considerably more mixing of the two symmetry coordinates is expected than for other halogen complexes.

A proper normal coordinate analysis to determine the force constants for this complex is not possible, since there are two experimental frequencies to determine three force constants, k_{II}, k_{NI}, and k_{12}, the interaction constant. Lake and Thompson assumed that the latter is zero; k_{II} is then about 1.13 mdyn/Å and $k_{NI} = 0.35$ mdyn/Å. Another reasonable assumption is $k_{12} = 0.4$ mdyn/Å (see ref 22); then $k_{II} = 1.51$ mdyn/Å and $k_{NI} = 0.37$ mdyn/Å. From this, we conclude that the force constant (1.25 mdyn/Å) calculated from the "diatomic molecule approximation" in Table IV may be a reasonable compromise estimate of k_{II} which, however, depends critically on the value for the interaction constant.

We note from these examples that k_{NI} is relatively independent of the choice of k_{12}; if the force constant k_{NI}^0 for the N–I bond in the pure dative structure *is* indeed relatively constant ($k_{NI}^0 \simeq 2.5$ mdyn/Å) for all amine·IY complexes as suggested previously,[22] the value of k_{NI} for the complex (0.35) could be used to estimate the weight of the dative structure, $b^2 + abS_{01}$; then k_{II} and k_{12} could be chosen to be consistent. From this procedure for pyridine·I_2, $k_{NI} \simeq 0.32$, $k_{II} \simeq 1.38$, $k_{12} \simeq 0.22$ mdyn/Å, and $b^2 + abS_{01}$ [from eq 1, or from $k_{NI} = k_{NI}^0(b^2 + abS_{01})$] is 0.13. For the 2,6-lutidine·I_2 complex, a similar procedure predicts $k_{II} \simeq 1.43$, $k_{NI} \simeq 0.27$, $k_{12} \simeq 0.29$ mdyn/Å, and $b^2 + abS_{01} \simeq 0.11$.

These estimates for the force constants seem quite reasonable, but the values of $b^2 + abS_{01}$ seem rather small when compared to other estimates of this quantity

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[21] The relationship between experimental properties of complexes and the coefficients of wave functions describing the complex have been discussed in many places, including ref 13. However, one should not take the actual values found for these coefficients *too* seriously; see R. S. Mulliken and W. B. Person in "Physical Chemistry," Vol. III, H. Eyring, W. Jost, and D. Henderson, Ed., Academic Press Inc., New York, N. Y., 1968, Chapter 11.

[22] Y. Yagi, A. I. Popov, and W. B. Person, *J. Phys. Chem.*, 71, 2439 (1967).

from dipole moments, for example. Still, they are not so unreasonable that they force us immediately to reject them. These estimates of $b^2 + abS_{01}$ are considerably smaller than the estimates from the "diatomic molecule approximation" in Table IV and eq 1.[23]

Examining Table IV, prejudiced by other[3] estimates of the "strength" of the complexes listed there, we might expect that the higher frequency is reasonably pure "I–I stretch" for all the complexes listed there, except possibly for $Et_2NH \cdot I_2$ and $Et_2S \cdot I_2$. These complexes are expected to have a rather strong D–I band, so that the band which is observed may actually be more nearly ν(D–I) than ν(I–I). Unfortunately, we cannot resolve this question without experimental information concerning the low-frequency vibrations for these complexes. We observed a weak band near 140 cm^{-1} for both complexes; it might possibly be the D–I stretching vibration. However, we think this band is not intense enough to be assigned to that motion. We do not find any other absorption for these complexes down to 100 cm^{-1}, however, suggesting that the mixing may still be small even for these strong complexes.

In spite of these many difficulties, it seems worthwhile to try to summarize in Table V the estimates for the I_2 complexes of the weight of the dative structure, $b^2 + abS_{01}$, obtained from eq 1 and the relative changes in the force constant, $\Delta k/k$. In Table IV, the frequency of I_2 in CCl_4 solution (207 cm^{-1}) is chosen as the reference frequency to fix k_{I-I}^0; in ref 22, k_{I-I}^0 is calculated from the gas-phase frequency (213 cm^{-1}). It would seem that the frequency of I_2 in an "inert" solvent, such as carbon tetrachloride, is probably the best choice; k_{I-I}^0 = 1.60 mdyn/Å. The resulting values of $\Delta k/k$ determine the estimates of $b^2 + abS_{01}$ which are listed in Table V. They differ somewhat from those listed earlier,[13] mostly due to changes in the choice of reference value, k_{I-I}^0, and also because of the attempts to estimate the mixing of the D–I and I–I vibrations. The agreement between different estimates of $b^2 + abS_{01}$ is about as good as can be expected.

Table V. Comparison of Estimates for the Weight of the Dative Structure ($b^2 + abS_{01}$) in Some I_2 Complexes

Complex	From $\Delta k/k$ in *n*-heptane (ref, ν 207 cm^{-1})	From μ
Benzene·I_2	0.02	0.044,[a] 0.11[b]
p-Dioxane·I_2	0.02	
Pyridine·I_2	0.13–0.29[c]	0.25[b]
Diethyl sulfide·I_2	0.17[e]–0.31[d]	
Diethylamine·I_2	0.31[d]	0.34[f]
Trimethylamine·I_2 (solid phase)	0.41[g]	
I_3^- (CsI_3) (solid phase)	0.44[g]	

[a] From Mulliken's estimate [R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952)] made using the data of F. Fairbrother, *J. Chem. Soc.*, 1051 (1948). [b] Using μ from the data of G. Kortüm and H. Walz, *Z. Electrochem.*, **57**, 73 (1953); see also K. Toyoda and W. B. Person, *J. Am. Chem. Soc.*, **88**, 1629 (1966) (in *n*-heptane) [c] The value depends on k_{12}; this range covers the "reasonable" values of k_{12} (see text) The most "reasonable" value is probably about 0.2. [d] Estimated using the "diatomic molecule approximation" and the frequency for ν(I–I) listed in Table IV. Probably too high (see text). [e] Estimated using the "triatomic molecule approximation" of ref 22, with ν(D–I) taken to be 140 cm^{-1} and with the interaction constant, k_{12}, assumed to be 0.40 mdyn Å (probably too low, see text). The alternate solution gives k_{II} for $Et_2S \cdot I_2$ as 0.92, so that $b^2 + abS_{01} \simeq 0.43$, which is more consistent, except for the peculiarly low intensity of the 140-cm^{-1} band (see text). [f] Estimated by S. Kobinata and S. Nagakura, *J. Am. Chem. Soc.*, **88**, 3905 (1966) (in benzene). [g] From "triatomic molecule approximation" given in ref 22.

Finally, let us consider the intensities for the I–I stretch. It is of some interest to compute the vibronic contributions to the intensity of the ν(I–I) band for these complexes.[13]

$$M_{\mathrm{N1,N0}} = (\partial\mu/\partial Q_1)_0 + \frac{2b(\partial E_{\mathrm{A}}^{\mathrm{v}}/\partial r)\mu_{\mathrm{EN}}}{a(m_{\mathrm{r}})^{1/2}\Delta W} = (\partial\mu/\partial Q_1)_0 + M \quad (2)$$

(Here these quantities have been defined earlier,[13] but see Table VI where some corrections to ref 13 are given.) The values of μ_{EN} and ΔW are estimated from the intensity and frequency of the electronic charge-transfer band for these complexes; b/a can be estimated from the values listed in Table V; $\partial E_A^v/\partial r$ has been estimated previously;[13] and m_r is the reduced mass of I_2.

From the values for these parameters listed in Table VI, the vibronic moment, M, is estimated [actually $M' = M(m_r)^{1/2}$] and compared in Table VI with the values of ϵ_a calculated using the "diatomic molecule approximation" from the observed intensities in Table IV. The agreement is quite good, except for the anomalous diethyl sulfide·I_2 and dioxane·I_2 complexes. The results calculated for pyridine·I_2 are in surprisingly good agreement with the experimental values. (Note that the calculated value for that complex here differs from the erroneous estimate given earlier.[13])

The mixing of the I–I symmetry coordinate with the N–I coordinate will, of course, affect the interpretation of the experimental intensities to obtain the experimental vibronic moment to be compared with M' so that the "diatomic approximation" ϵ_a is not the proper quantity to compare. As a result of the mixing, the normal coordinate for the higher "I–I" frequency, Q_1, contains contributions from both R_1, the change in the I–I frequency bond length, and R_2, the change in the N–I bond length.

$$\begin{aligned} Q_1 &= L_{11}^{-1}R_1 + L_{12}^{-1}R_2 \\ Q_2 &= L_{21}^{-1}R_1 + L_{22}^{-1}R_2 \end{aligned} \quad (3)$$

Here Q_2 is the normal coordinate associated with the lower frequency "N–I" vibration. Using the force constants from Lake and Thompson[12] (k_{12} = 0), we compute

$$L^{-1} = \begin{bmatrix} 9.08 & -1.99 \\ 6.86 & 9.79 \end{bmatrix} \times 10^{-12} \quad (4)$$

From this and the relationship

$$\partial\mu/\partial R_i = \sum_i L_{ij}^{-1}(\partial\mu/\partial Q)_i \quad (5)$$

we may compute $\partial\mu/\partial R_j$ from the intensities given by

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(23) These arguments, complicated as they may be here, are still somewhat oversimplified. For example, negative values of k_{12} may be possible. There are always two sets of force constants: one with high k_{II} and low k_{NI} and one with the opposite result. We reject one on the basis that it is "unreasonable." We do not wish to extend this discussion unnecessarily, since we understand that Lake and Thompson are attempting a more careful study of normal coordinates and force constants of these complexes (private communication).

Table VI. Comparison of Calculated and Observed Vibronic Moments for the I–I Stretching Vibration of Some Complexes

Complex	ΔW,[a] eV	μ_{EN}[b]	$(\partial E_A{}^v/\partial r)$[c,g] × $(\mu_{EN}/\Delta W)$	$(b^2 + abS_{01})$[d]	a	b	M′,[e] D/Å	ϵ_a,[f] D/Å
Benzene·I_2	4.24[g]	4.8[g]	+4.81	0.02	0.99	0.10	0.97	1.5
p-Dioxane·I_2	4.72[h]	2.3[h]	+2.07	0.02	0.99	0.10	0.42	3.2
Pyridine·I_2	5.26[g]	7.5[g]	+6.05	0.29	0.78	0.43	6.7	5.6
3-Picoline·I_2	*i*	*i*	*i*	*i*	*i*	*i*	*i*	*i*
2,6-Lutidine·I_2	*i*	*i*	*i*	*i*	*i*	*i*	*i*	*i*
Diethyl sulfide·I_2	4.09[j]	6.6[j]	+6.86	0.35	0.73	0.49	9.2	4.7
Diethylamine·I_2	4.80[k]	5.9[k]	+5.22	0.35	0.73	0.49	7.0	>3.2

[a] $\Delta W = \nu_{CT}/8066$ eV. [b] $\mu_{EN} = [(0.92 \times 10^{-2}/\nu_{CT})\epsilon_{max}\Delta\nu_{1/2}]^{1/2}$ D. [c] Note that the sign of $\partial E_A{}^v/\partial r$ is given *erroneously* in ref 13 as negative. [d] Estimated from $\Delta k/k$; selected from Tables IV and V. These numbers are quite uncertain (see Table IV); however, the values chosen here give an idea of the magnitude of M'. We have arbitrarily chosen the upper limit of the range shown in Table V for the pyridine·I_2 complex. $S_{01} = 0.1$ for complexes with benzene and dioxane; $S_{01} = 0.3$ for other complexes here. [e] M' is obtained from $M_{N1,N0}$ by multiplying by $(m_r)^{1/2}$; to convert from the values given in ref 13, m_r is in atomic mass units; generally, of course, it is in units of grams. M' should be equal to ϵ_a if the "diatomic molecule approximation" is valid; if it fails, then M' should be compared with $\partial\mu/\partial R_1$. [f] "Diatomic approximation" ϵ_a values from Table IV. See discussion in the text for the pyridine·I_2 complex. [g] From Friedrich and Person, ref 13. [h] From J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit, and W. Dzcubus, *Rec. Trav. Chim.*, **71**, 1104 (1952). [i] Assumed to be the same as for pyridine·I_2. [j] From H. Tsubomura and R. P. Lang, *J. Am. Chem. Soc.*, **83**, 2085 (1961). [k] From H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc., Japan*, **33**, 1660 (1960).

Lake and Thompson[12] (to get $\partial\mu/\partial Q_2$) for pyridine·I_2. We find

$$\partial\mu/\partial R_1 = 10.17 \text{ or } 1.53 \text{ D/Å}$$

$$\partial\mu/\partial R_2 = 4.87 \text{ or } -7.45 \text{ D/Å}$$

Here the first choice in each case is correct if the two dipole derivatives, $\partial\mu/\partial Q_i$, have the same signs; the second choice is correct if they have opposite signs. We have arbitrarily chosen $\partial\mu/\partial Q_1$ positive; if it is negative, we must change all signs.

The two values of $\partial\mu/\partial R_1$ may be compared with ϵ_a = 5.6 D/Å from Table IV. The agreement here for either choice of signs is bad so that the mixing of the "I–I" and the "N–I" stretching symmetry coordinates must not be ignored in computing the experimental value of the "vibronic moment" for this vibration.

However, the value of k_{12} has a considerable influence on the normal coordinates. In order to investigate the effect of k_{12}, we may consider the normal coordinates computed from the other two sets of force constants discussed above, with $k_{12} \simeq 0.4$ and with $k_{12} \simeq 0.22$ mdyn/Å. From set 1, with $k_{12} \simeq 0.4$, we find

$$L^{-1} = \begin{pmatrix} 11.18 & 2.47 \\ 2.31 & 9.69 \end{pmatrix} \times 10^{-12} \qquad (6)$$

From set 2, with $k_{12} \simeq 0.22$, we find

$$L^{-1} = \begin{pmatrix} 10.57 & 0.67 \\ 4.28 & 9.97 \end{pmatrix} \times 10^{-12} \qquad (7)$$

Using these to compute the values of $\partial\mu/\partial R_j$ in eq 5, we find for set 1 ($k_{12} \simeq 0.4$)

$$\partial\mu/\partial R_1 = +8.66 \text{ or } 5.76 \text{ D/Å}$$

$$\partial\mu/\partial R_2 = 7.69 \text{ or } -4.49 \text{ D/Å}$$

for set 2 ($k_{12} \simeq 0.22$)

$$\partial\mu/\partial R_1 = 9.52 \text{ or } 4.12 \text{ D/Å}$$

$$\partial\mu/\partial R_2 = 6.71 \text{ or } -5.85 \text{ D/Å}$$

Thus, there is considerable variation in $\partial\mu/\partial R_j$, depending upon the particular set of force constants chosen.

If the vibronic terms are dominant in determining $\partial\mu/\partial R_i$, then we expect $\partial\mu/\partial R_1$ to be positive and $\partial\mu/\partial R_2$ to be negative. The argument is as follows. When the I–I bond is stretched, the electron affinity increases, so that the structure py$^+$–$(I_2)^-$ becomes favored, *increasing* μ. Therefore $\partial\mu/\partial R_1$ is positive since R_1 is positive if the I–I band increases in length, and since that change causes μ to increase. On the other hand, when we stretch the N–I bond (R_2 positive), the overlap integral decreases in size, favoring the no-bond structure py···I_2, and *decreasing* μ. Therefore $\partial\mu/\partial R_2$ is expected to be negative.

Examining the solutions above, we find that the choice of opposite signs for $\partial\mu/\partial Q_i$'s gives opposite signs for the $\partial\mu/\partial R_j$'s. In fact the values of $\partial\mu/\partial R_j$ calculated from this sign choice for the $\partial\mu/\partial Q_i$'s are quite reasonable, especially for k_{12} somewhat greater than zero. The values either for $k_{12} = 0.22$ or for $k_{12} = 0.4$ give a value of $\partial\mu/\partial R_1$ which is in excellent agreement with the calculated value of M' (Table VI). It is apparent that the value of $\partial\mu/\partial R_2$ associated with stretching the N–I bond is almost as large in magnitude as for $\partial\mu/\partial R_1$ for the I–I bond, suggesting that the effect of changing overlap on the infrared intensity is indeed quite large for these complexes. The agreement between the "diatomic approximation" ϵ_a and the value of $\partial\mu/\partial R_1$ calculated from force constant set 1 is apparently fortuitous.

In view of the uncertainty in the normal coordinates due to the lack of sure knowledge about k_{12} it seems useless to carry this discussion further at present. The results for the iodine complexes may all be quite consistent with the theory,[13] although the anomalous value for the intensities of the dioxane·I_2 complex raises immediate and difficult questions about the theory. However, more data are needed for these systems, particularly concerning ν(N–I), before the anomalies can be explained.

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