

Resolution of the Far Ultraviolet Absorption Bands of Solvated Iodide

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The far u.v. absorption band profiles of iodide dissolved in a variety of solvents have been deconvoluted using a comprehensive computer program. Several different approaches are incorporated within the overall program, including an iterative least mean squares minimization method for a combination of linear normal (Gaussian) curves, and another similar method which uses instead a linear combination of log-normal curves. The results obtained using the separate approaches demonstrate that the absorption spectra of solvated iodide are comprised of sets of band pairs arising from the $^2P_{3/2} - ^2P_{1/2}$ iodide radical doublet.

In a previous report¹ we presented preliminary results on the far ultraviolet spectra of iodide ions in some solvents at wavelengths down to 165 nm ($61\,000\text{ cm}^{-1}$). All the solvated iodide spectra showed well-defined bands at low energy, merging into relatively bland high-intensity absorption profiles at higher energies [see e.g., fig. 1 in ref. (1)]. The investigation has been extended to cover a very wide range of solvents and temperatures.² The resolution methods used previously¹ to obtain the component bands of the solvated iodide included an analogue method using a du Pont curve resolver, and a simple analytical method called DECON, described separately.³

The resolved spectra showed the presence of two sets of doublets, referred to as the A_1/A_2 and the B_1/B_2 band pairs, as well as additional bands in the far u.v. (D etc.). The second set of doublets B_1 and B_2 , which were observed^{1, 2} for the first time, were not predicted in the theory of charge-transfer-to-solvent (c.t.t.s.) spectra of halide ions.⁴ In response to some reservations expressed on the resolution methods used, we have developed further computer methods using as starting points the methods used by Schwartz⁵ and by Siano and Metzler.⁶ The first method is an iterative least mean squares minimization method for a linear combination of normal (Gaussian) curves, called GSAN in this work. The second method, called LOGFIT, is similar but uses instead a linear combination of log-normal curves, the ratio of the half-half widths at half-height being an additional variable, ρ . The input information to these programs is the experimental data obtained either from the du Pont curve resolver, the DECON method, or from a differential method, PEAK.⁷

The advantages obtained through minimisation methods like GSAN or LOGFIT lie in the small adjustments made in the band parameters by the iterative procedure which reduces the discrepancy between the experimental and the synthesized absorption profiles, measured by the root mean square (r.m.s.) value, until a local minimum is found. A further advantage of using both GSAN and LOGFIT is

that a comparison may be made between the use of symmetric and asymmetric absorption profiles, a point of previous discussion.^{6, 8} Convergence of the procedure was obtained using either Newton's method⁹ or the steepest descent method,¹⁰ the former being continually monitored for true convergence. With a maximum of 18(GSAN) or 24(LOGFIT) independent variables it is essential that a constant, apparently minimum, r.m.s. value is checked to be the true convergence limit, for this may be just an interim result en route to the final minimum. For this reason we have set the criterion for a convergence limit as being 5 constant r.m.s. values for successive iterations and this value remains unaltered when the convergence method was changed to the alternative approach. The latter condition is essential when a large number of variables are involved in the minimisation procedure. A limitation of GSAN and LOGFIT is that they are not capable of guaranteeing that the result is a true global minimum; at the present stage of development this must be left to the (experienced) intuition of the user.

EXPERIMENTAL

The absorption profiles analysed in this work were obtained using techniques described previously.^{1, 2, 11} The analytic program was developed from listings kindly supplied by Schwartz⁵ and by Siano and Metzler.⁶ The program was used on a Honeywell DDP 516 with 16K core, disc store and graphical visual display peripherals.

RESULTS

We have selected extremes of spectra for this analysis. Extreme in the sense that the iodide absorption bands are strongly blue-shifted or strongly red-shifted by the

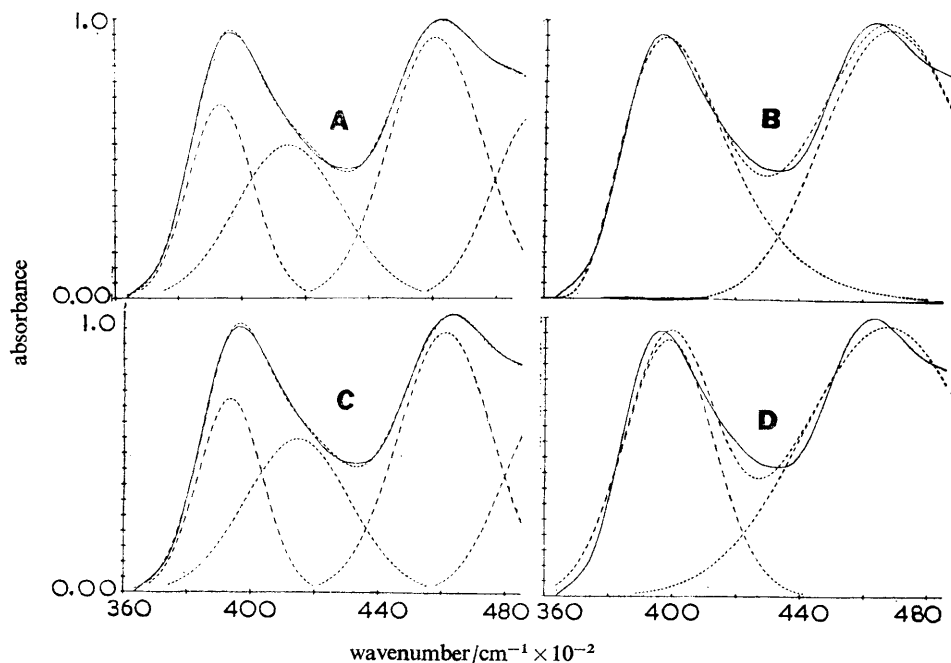


FIG. 1.—U.v. absorption profile of iodide (as the tetramethylammonium salt at 5×10^{-3} mol dm⁻³) in acetone at 180 K (full line). Resolution strategy involving; (A) four normal curves (GSAN), r.m.s. = 0.0060; (B) two normal curves (GSAN), r.m.s. = 0.0463; (C) four lognormal curves (LOGFIT), r.m.s. = 0.0056; (D) two lognormal curves (LOGFIT), r.m.s. = 0.0265. Dotted lines along the experimental curve for iodide show the reconstituted sum of the resolved curves.

TABLE 1.—ABSORPTION BAND PARAMETERS OF IODIDE IN VARIOUS SOLVENTS RESOLVED USING THE NORMAL AND LOGNORMAL BANDSHAPE METHODS

system resolution method	r.m.s. value	A ₁		B ₁	
acetone, 180 K					
GSAN, 4 bands	0.006 0	41 203	0.695	2381	
GSAN, 2 bands	0.046 3	41 752	0.921	3320	
LOGFIT, 4 bands	0.005 6	41 187	0.696	2393	1.02
LOGFIT, 2 bands	0.026 5	41 614	0.942	5274	1.48
acetone, 318 K					
GSAN, 5 bands	0.004 1	38 509	0.335	2824	
GSAN, 3 bands	0.020 6	38 379	0.504	4079	
LOGFIT, 4 bands	0.004 8	38 807	0.457	3300	1.07
LOGFIT, 3 bands	0.013 0	39 310	0.521	4456	1.27
butyronitrile, 153 K					
GSAN, 5 bands	0.004 1	42 907	0.484	2267	
GSAN, 3 bands	0.019 5	42 993	0.492	2487	
LOGFIT, 5 bands	0.004 3	42 896	0.486	2297	1.03
LOGFIT, 3 bands	0.013 1	42 879	0.496	2443	1.18
butyronitrile, 318 K					
GSAN, 5 bands	0.002 2	39 911	0.560	2992	
GSAN, 3 bands	0.015 0	40 030	0.521	2955	
LOGFIT, 5 bands	0.003 0	39 888	0.570	3016	1.03
LOGFIT, 3 bands	0.005 1	39 917	0.552	3138	1.13
D ₂ O, 318 K					
GSAN, 4 bands	0.004 7	44 466	0.721	4199	
GSAN, 3 bands	0.005 3	44 412	0.710	4110	
LOGFIT, 4 bands	0.004 6	44 442	0.721	4233	1.04
LOGFIT, 3 bands	0.006 3	44 412	0.710	4110	1.01
		43 329	0.551	3877	
		43 326	0.551	3894	1.02
		40 966	0.408	4259	
		41 791	0.352	3977	1.05
		47 619	0.171	5346	
		46 901	0.146	4605	1.10
		44 171	0.251	6010	
		44 079	0.253	5543	1.01
		55 513	0.363	5356	
		55 077	0.415	7357	1.27

		A_2		B_2		D	
acetone, 180 K							
	GSAN, 4 bands	0.006 0	47 967 0.936 3500	51 129 0.662 3250			
	GSAN, 2 bands	0.046 3	48 612 0.971 6231				
	LOGFIT, 4 bands	0.005 6	47 971 0.937 3490 1.03	51 129 0.661 3261 1.02			
	LOGFIT, 2 bands	0.026 5	48 646 0.973 5274 1.13				
acetone, 318 K							
	GSAN, 5 bands	0.004 1	45 800 0.572 4633	50 891 0.699 6654	53 178 0.466 3 848		
	GSAN, 3 bands	0.020 6	45 831 0.577 6752		55 261 1.077 10 772		
	LOGFIT, 4 bands	0.003 7	45 898 0.584 4215 1.03	50 990 0.778 6463 1.04			
	LOGFIT, 3 bands	0.013 0	45 641 0.530 5478 0.90		51 560 0.750 8 478 1.13		
butyronitrile, 153 K							
	GSAN, 5 bands	0.004 1	49 811 0.317 2800	52 607 0.290 5899	56 743 0.380 4 992		
	GSAN, 3 bands	0.019 5	49 833 0.530 4902		55 985 0.475 5 532		
	LOGFIT, 5 bands	0.004 3	49 779 0.399 3127 1.03	50 715 0.531 7177 1.12	56 176 0.718 66 348 1.00		
	LOGFIT, 3 bands	0.013 1	50 005 0.564 4518 0.87		55 620 0.478 6 407 1.43		
butyronitrile, 318 K							
	GSAN, 5 bands	0.002 2	46 971 0.474 3262	50 834 0.520 6667	56 191 0.768 6 631		
	GSAN, 3 bands	0.015 0	46 803 0.404 3367		57 860 0.930 20 054		
	LOGFIT, 5 bands	0.003 0	46 897 0.472 3212 1.03	50 715 0.531 7177 1.12	56 176 0.718 6 634 1.00		
	LOGFIT, 3 bands	0.005 1	46 893 0.410 3407 0.87		59 538 0.963 27 158 1.37		
D ₂ O, 318 K							
	GSAN, 4 bands	0.004 7	51 470 0.671 4190		59 059 0.771 5 274		
	GSAN, 3 bands	0.005 3	51 429 0.600 4082		59 727 0.977 10 025		
	LOGFIT, 4 bands	0.004 6	51 263 0.500 3951 1.01		59 180 0.680 5 895 1.11		
	LOGFIT, 3 bands	0.003 3	51 464 0.546 3841 0.99		59 284 0.951 8 564 0.7		

For each band, results are given in the order of $\nu_{\max}/\text{cm}^{-1}$, band height in absorbance units, and half-width, $\nu_{\frac{1}{2}}/\text{cm}^{-1}$. The asymmetry ρ , is given where appropriate.

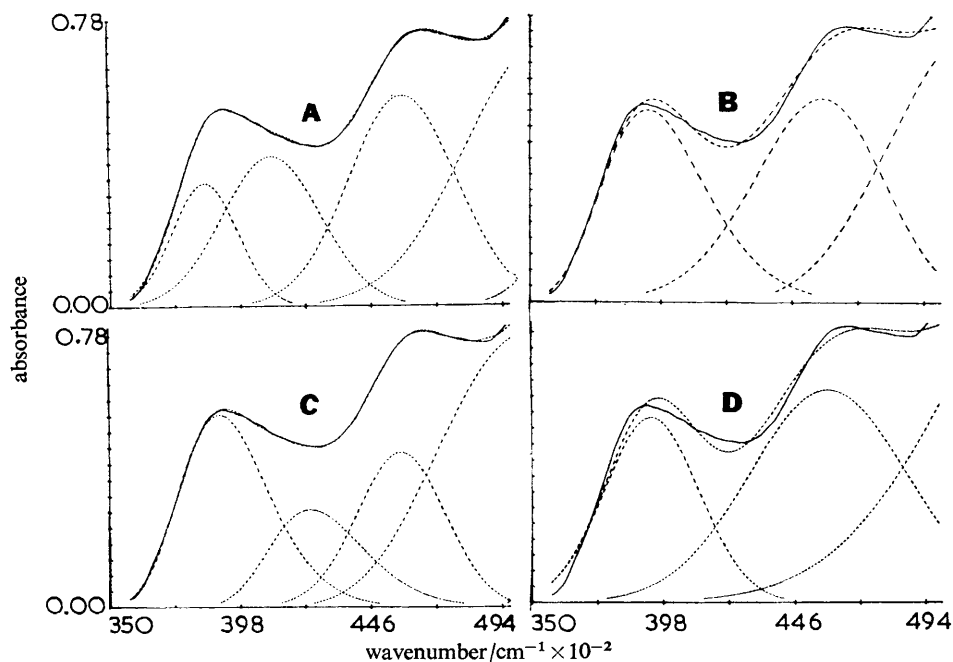


FIG. 2.—U.v. absorption profile of iodide (as the tetramethylammonium salt at 5×10^{-3} mol dm $^{-3}$) in acetone at 318 K (full line). Resolution strategy involving: (A) five normal curves (GSAN), r.m.s. = 0.004 1; (B) three normal curves (GSAN), r.m.s. = 0.020 6; (C) four lognormal curves (LOGFIT), r.m.s. = 0.003 7; (D) three lognormal curves (LOGFIT) r.m.s. = 0.013 0.

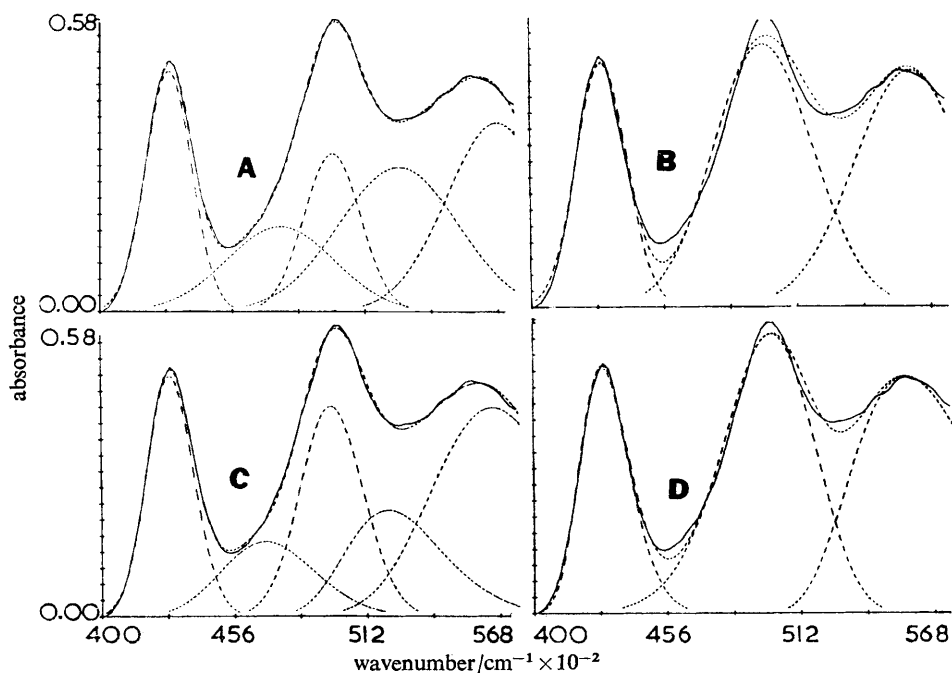


FIG. 3.—U.v. absorption profile of iodide (as the tetramethylammonium salt at 5×10^{-3} mol dm $^{-3}$) in butyronitrile at 153 K (full line). Resolution strategy involving: (A) five normal curves (GSAN), r.m.s. = 0.004 1; (B) three normal curves (GSAN), r.m.s. = 0.019 5; (C) five lognormal curves (LOGFIT), r.m.s. = 0.004 3; (D) three lognormal curves (LOGFIT), r.m.s. = 0.013 1.

solvent and/or by temperature.¹ The solvents have also been chosen for their different polar character, i.e., a nitrile, a ketone and water. We pose the problem as that of fitting symmetric or asymmetric normal curves to a given experimental absorption profile using (1) the presence of the B_1/B_2 band pair, and (2) not using this band pair.

This approach is illustrated in fig. 1 for the best-fitted absorption profiles of iodide in acetone at 180 K for (A) four components, normal (symmetric), GSAN, (B) two components, normal, GSAN, (C) four components, lognormal, LOGFIT, and (D) two components, lognormal, LOGFIT. The respective r.m.s. values are 0.006 0, 0.046 5, 0.005 6 and 0.026 5, demonstrating that four peak combinations using both methods give much closer solutions than the two peak combinations. The r.m.s. value is lower for the two-peak lognormal than for the analogous normal combination because of the large asymmetry of the bands. The bands parameters are given in table 1.

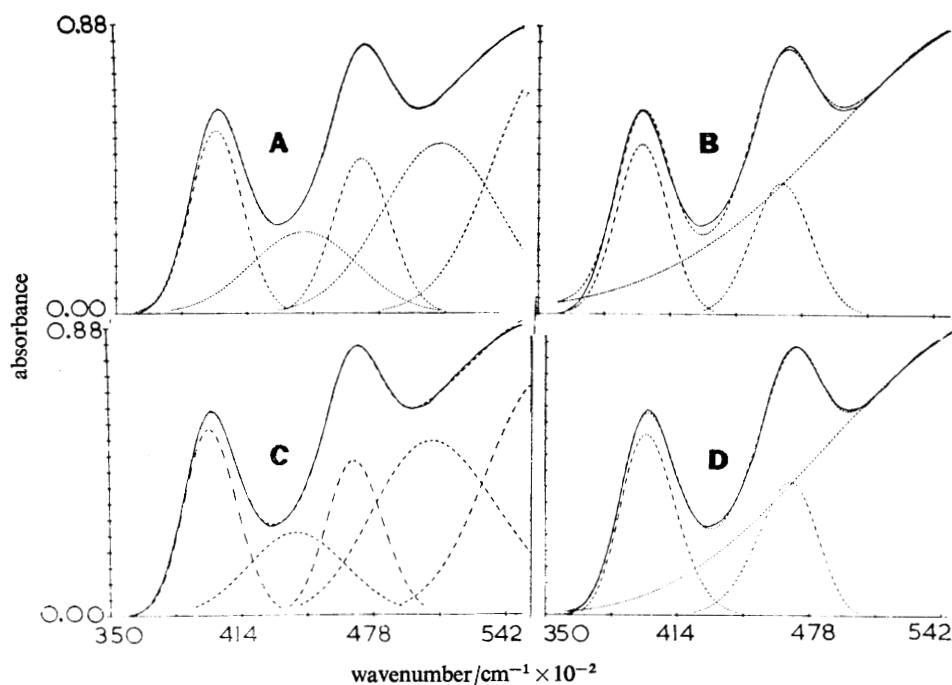


FIG. 4.—U.v. absorption profile of iodide (as the tetramethylammonium salt at 5×10^{-3} mol dm⁻³) in butyronitrile at 318 K (full line). Resolution strategy involving: (A) five normal curves (GSAN), r.m.s. = 0.002 2; (B) three normal curves (GSAN), r.m.s. = 0.015 0; (C) five lognormal curves (LOGFIT), r.m.s. = 0.003 0; (D) three lognormal curves (LOGFIT), r.m.s. = 0.005 1.

On increasing the temperature to 318 K, the experimentally determined absorption profile of iodide in acetone changes considerably, see fig. 2, and is also red-shifted. The spectrum can be equally well resolved as at 180 K, albeit the spectral parameters of the A_1 , A_2 , B_1 etc. bands are significantly different, table 1.

The solvation of iodide ions in butyronitrile gives rise to different absorption profiles, compared to those in acetone as solvent. The resolved bands in this case clearly show the presence of the two pair of doublet bands, figs 3 and 4. The A_1 , A_2 and the B_1 , B_2 band pairs have similar spectral characteristics (e.g. width at half peak

height) but they differ from each other in their response to temperature and solvent charge. For those spectra where the region of measurement extends further into the far ultraviolet another higher energy peak (D) is included, the distinction then being made is between three- and five-bands solutions.

For iodide in D₂O the B₁/B₂ band pair is sufficiently blue-shifted relative to the A₁/A₂ pair that the B₂ band is beyond the range of measurement, fig. 5. Again, the lowest r.m.s. values are obtained by including B₁ into a linear combination of bands. The variation between the various assemblies of band components is less in this case than for those where both B₁/B₂ can be observed, the decrease arising from the influence of another band where, in the absence of B₁, a substantial contribution of the absorption profile can be given by an extremely broad band, together with a dramatically reversed ratio for ρ (for lognormal curves).

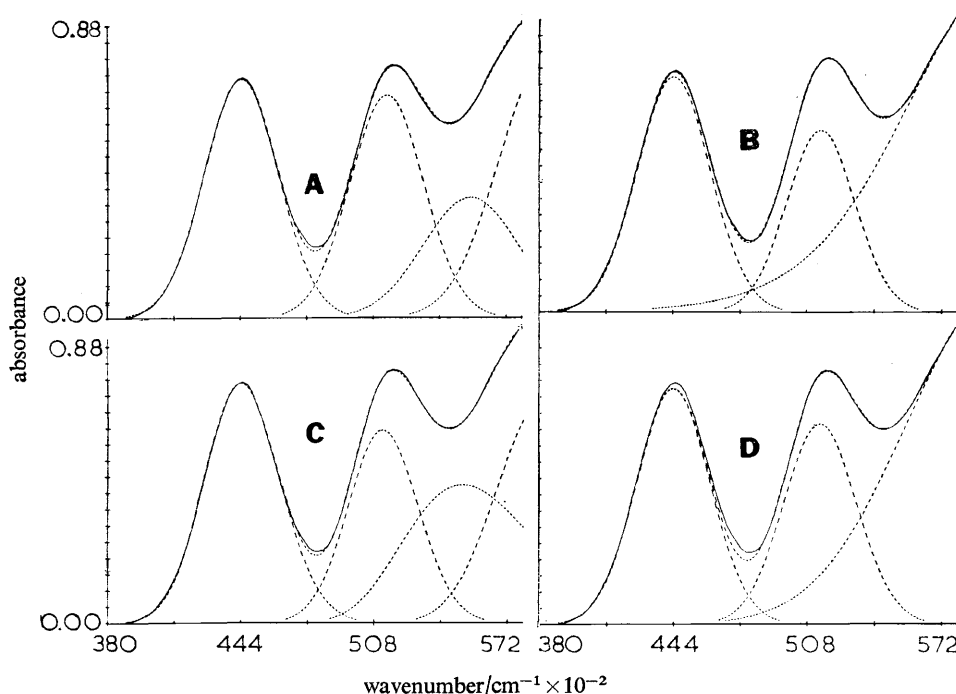


FIG. 5.—U.v. absorption profile of iodide (as the tetramethylammonium salt at 5×10^{-3} mol dm⁻³) in D₂O at 318 K (full line). Resolution strategy involving: (A) four normal curves (GSAN), r.m.s. = 0.047; (B) three normal curves (GSAN), r.m.s. = 0.005 3; (C) four lognormal curves (LOGFIT), r.m.s. = 0.004 6; (D) three lognormal curves (LOGFIT), r.m.s. = 0.006 3.

DISCUSSION

If it is assumed that the far u.v. absorption profile of iodide arises from a set of discrete transitions and, further, that those transitions may be represented by normal or log-normal curves, then a low value (comparable to errors in the experimental spectrum profile) or a zero r.m.s. value for a synthesised spectrum confirms the former as a description of the transitions involved. Whilst use of additional bands will improve a solution to the problem, and a large number would give an ideal solution, we have constrained the number of bands to a minimum number consistent with theoretical models. It is clear from table 1 that the lowest r.m.s. values occur

when the B_1/B_2 band pair (or B_1 alone) are included in the linear combination of band shapes. When only A_1 and A_2 (and an additional high-energy band where necessary) are included an acceptably low r.m.s. value is obtained only for values of ρ which are significantly different from unity, and often in different directions, e.g., for A_1/A_2 for iodide in butyronitrile at 153 K, ρ has values of 1.18 and 0.87 for the combination which does not include the B_1/B_2 band pair. The close similarity between the A_1 and A_2 band pair properties has always been a fundamental characteristic leading to recognition of the doublet nature of the transitions. To a good first approximation, the energy difference between the A_1 and A_2 transitions can be assigned to the difference between the $^2P_{3/2}$ and $^2P_{1/2}$ terms of the iodide atoms produced in the excited state of the transition. If the asymmetry of the band reflects the relationship of the ground and the excited state potential energy curves, as has been argued by Siano and Metzler,⁶ then it would be physically unreasonable for the two components of a doublet to have such radically different values of ρ . On the other hand, when the B_1/B_2 band pair are included, values for the A_1/A_2 band pair are close to unity and also very close to each other. Values of ρ for the B_1/B_2 band pair, whilst being slightly larger than those for A_1/A_2 , are also generally close to each other, as would appear reasonable for a doublet transition pair. The value of ρ found for the A_1 band of iodide in D_2O , 1.04, is in excellent agreement with the value found for iodide in H_2O by Siano and Metzler.⁸ There is some disagreement with their value for A_2 , 0.98. In this work a value of 1.01 is obtained by using an absorption profile which extends much further into the ultra-violet region.

The separation of B_1 and B_2 is of the same order of magnitude as that for A_1 and A_2 , and would indicate that these bands also arise from $^2P_{3/2}$ and $^2P_{1/2}$ states of iodine. In support of this assignment is the knowledge that there are no higher bound states for iodide, and higher states of iodine atoms lie at very much higher energies. Therefore, to a first approximation, the B doublet arises from the iodine atom ground state doublet and a higher energy solvated electron state. In conventional c.t.t.s. spectroscopy theories, the solvated electron state lies in a spherical potential well with either a $1s$ or $2s$ function describing the electron distribution.⁴ If the A band set is regarded as arising from the ns electron state, then the B set may be regarded as arising from the $(n+1)s$ electron state. Detailed analysis of the temperature and solvent sensitivities of the B doublet, as also of the higher energy band D, etc., is in progress.²

One problem in computer deconvolution is that there are rarely unique solutions for the multi-parameter functions discussed in this work. Therefore, a solution is generally described by a surface in n -dimensional space which has, to take a very much simplifying visual approach in two dimensions, a shallow minimum condition. For n -dimensions this means that different approaches can give r.m.s. values which are similar but for which the grouped parameters, i.e., those for each band may be somewhat different between the approaches used. Whilst this situation should not arise for absorption envelopes composed of synthesised curves, the real absorption envelopes are composed of approximately Gaussian shapes together with a real error component introduced in the recording and transposition of the data. For the real cases discussed in this work it can be seen that the bands which are strongly overlapped may "feed" off each other by a mutual process. Such effects are less marked for band positions but do occur in some cases for band widths and heights. Clearly this is a problem related to that of the limits of accurate resolution as discussed by Barker *et al.*³ and by Morrey.⁷

In conclusion, by comparison of the goodness of fit obtained for computer

deconvolution approaches where an additional 2P double pair transition is either included or excluded from iodide absorption spectra in various solvents, it has been demonstrated that the additional doublet pair are real. The proposal of a series of electron states in iodide solution spectra is analogous to the series of states proposed for the spectra of pure rare gases, dilute solid rare gas spectra and the spectra of alkali metal halides in the far u.v.¹²

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