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Far-ultraviolet Solution Spectroscopy of Thiocyanate

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The far-ultraviolet solution of very dilute thiocyanate ion in a range of solvents shows that there are at least three absorption bands labelled A, D and E. All three bands are shown to have charge-transfer-to-solvent characteristics, in contrast to some previous reports. The conflicting previous reports of the spectroscopy and photochemistry of thiocyanate ions, together with the current work, are resolved in terms of a spectroscopic transition scheme involving a forbidden transition at *ca.* 36 000 cm^{-1}, which is normally extremely weak or not detectable. This transition is only detected at high concentrations of salt. The first allowed transition is expected to occur at *ca.* 62 000 cm^{-1}. Within this scheme the c.t.t.s. bands occur (in aqueous solution) at 46 000 and 53 500 cm^{-1}. A further band is observed in red-shifting solvents at *ca.* 57 000 cm^{-1}. The temperature sensitivities of the three c.t.t.s. bands, relative to the solvated electron, are 0.58, 0.47 and 0.30.

There is an unresolved discontinuity in the experimental spectroscopy, photochemistry and theoretical chemistry of the thiocyanate ion. On the one hand, McGlynn and coworkers[1] have assigned the 46000 cm^{-1} (220 nm) absorption band of thiocyanate in aqueous solution to a $\pi \rightarrow \pi^*$ transition, by analogy to the spectra of HNCS and the isoelectronic species carbon disulphide. The phosphorescence and excitation spectra of the thiocyanate salts of heavy metals in aqueous and alcoholic solid solution at 77 K were additional factors in deciding that the transition was of an internal, intramolecular transition.

On the other hand, Di Sipio *et al.*[2] have shown that the first allowed transition of thiocyanate would occur at 65000 cm^{-1}. Treinin and coworkers[3] have shown that the same absorption band of thiocyanate in water has strong charge-transfer-to-solvent (c.t.t.s.) character. The band shifts to higher or lower energies when the ion is placed in blue- or red-shifting solvents, respectively, precisely as would be expected for a c.t.t.s. transition. Finally, the first thiocyanate absorption maximum at *ca.* 46000 cm^{-1} in water fits in very well with a correlation, drawn by Treinin and coworkers,[3] between the energy of the first absorption maximum and the electrochemical decomposition voltage of 0.1 KX, where X is a halide. The halide transitions are the indisputable archetypes of c.t.t.s. spectroscopy.[4-9]

Dogliotti and Hayon[10] showed that the photochemistry of aqueous thiocyanate could be divided into two processes, one occurring above *ca.* 240 nm and the other below. The first is shown to be due to an internal transition and the latter to an external c.t.t.s. transition, the generation of a solvated electron being very good evidence for the latter process.

Several developments offer the possibility of investigating the spectroscopy of thiocyanate from fresh standpoints. First, the extension of conventional solution spectroscopic techniques into the far-ultraviolet region, down to 168 nm (59500 cm^{-1}) for some solvents.[11] Secondly, the ability to extend drastically the range of solvents and temperatures for which spectra may be obtained.[6-9, 12] Thirdly, computer deconvolution techniques of the observed spectra which can separate out the individual bands contributing to the absorption profile.[13] We now bring these three techniques together to look again at the ultraviolet solution spectra of the thiocyanate ion.

EXPERIMENTAL

The particular techniques used for the study of the ultraviolet spectroscopy of solutions, at low and ambient temperatures, have been extensively described in our previous papers on the halides and hydrosulphide.[6-9] We emphasise that these spectra are independent of anion concentration (up to 8×10^{-3} mol dm^{-3}) and also independent of cation in all the solvents used. Solvents were either spectroscopic grade or purified according to previously described techniques.[4] The thiocyanate salts were either potassium, ammonium or tetramethylammonium thiocyanates, all Eastman Kodak. Spectra were obtained using a Cary 15 'low-u.v.' model and transcribed by hand into a computer file. A SP700 was also used for normal u.v. spectra. Spectra were deconvoluted using the DECON program of Leicester Polytechnic.[13]

The spectra are composed of broad, well-overlapped bands and we would normally prefer to use lognormal, asymmetric band functions as we have in previous work.[6-9] However, the absorption profiles may be described as being broad in character, even for the low temperature spectra shown in fig. 1. We found that the asymmetry parameters varied aimlessly in the convergence procedure, *i.e.* the convergence minimum surface in hyperspace is broad and shallow. Therefore, we chose to use a linear summation of symmetric Gaussians to the observed profile as a simpler and more meaningful approach to this type of spectrum.

RESULTS

We commence by analysing[13] the relatively well-known spectrum of thiocyanate in aqueous solution at 274 K, fig. 1 (*a*). The higher energy band whose absorption was observed in earlier studies is now fully observed as a peak at 53989 cm^{-1}, in addition to the first band at 46204 cm^{-1}. The oscillator strengths are 0.395 and 0.066 for the higher and lower energy bands, respectively. The band maxima, $\nu_{\max}$, shift to lower energies with a temperature coefficient, $d\nu_{\max}/dT$, of -13.5 cm^{-1} K^{-1} for the lower energy band and -36.5 cm^{-1} K^{-1} for the second, more intense, band.

We designate these bands A and D, by analogy to the halide band systems in the far-ultraviolet region. There is good evidence for a further band, E, at higher energies, 57599 cm^{-1}, with an oscillator strength of 0.414. These results are entirely consistent with deconvolution results for solution temperatures over the range 274–318 K.

We now consider the spectra of thiocyanate in a range of solvents over an extended range of temperatures. For the red-shifting solvents, we have used[11] acetone over the range 208-318 K, acetonitrile (230-318 K), propionitrile (200-318 K), triethyl phosphate (212-318 K) and dimethoxyethane (214-318 K).

The low-temperature spectra of thiocyanate are shown in propionitrile at 200 K, fig. 1 (*b*), and in triethylphosphate at 212 K, fig. 1 (*c*), both spectra demonstrating the three absorption band system found previously in aqueous solution and labelled similarly. For these two examples, band A is at *ca.* 45000 cm^{-1}, B at *ca.* 52500 cm^{-1} and E at 57000 cm^{-1}.

We draw attention at this stage to the spectra of thiocyanate in liquid ammonia from 293.6 to 326.4 K, published by Treinin and coworkers,[3] which is paralleled by the spectrum of iodide in the same solvent at the same temperatures.

For blue-shifting solvents, we have used iso-butanol (258-318 K) and trifluoroethanol and hexafluoropropan-2-ol (270-318 K). For these solvents the band system has been substantially shifted, *e.g.* band A shifts from 42845 cm^{-1} in acetone to 53083 cm^{-1} in hexafluoropropan-2-ol at 270 K. It is therefore much more difficult to see the third band due to limitations caused by either the spectroscopic limit of the solvent or the

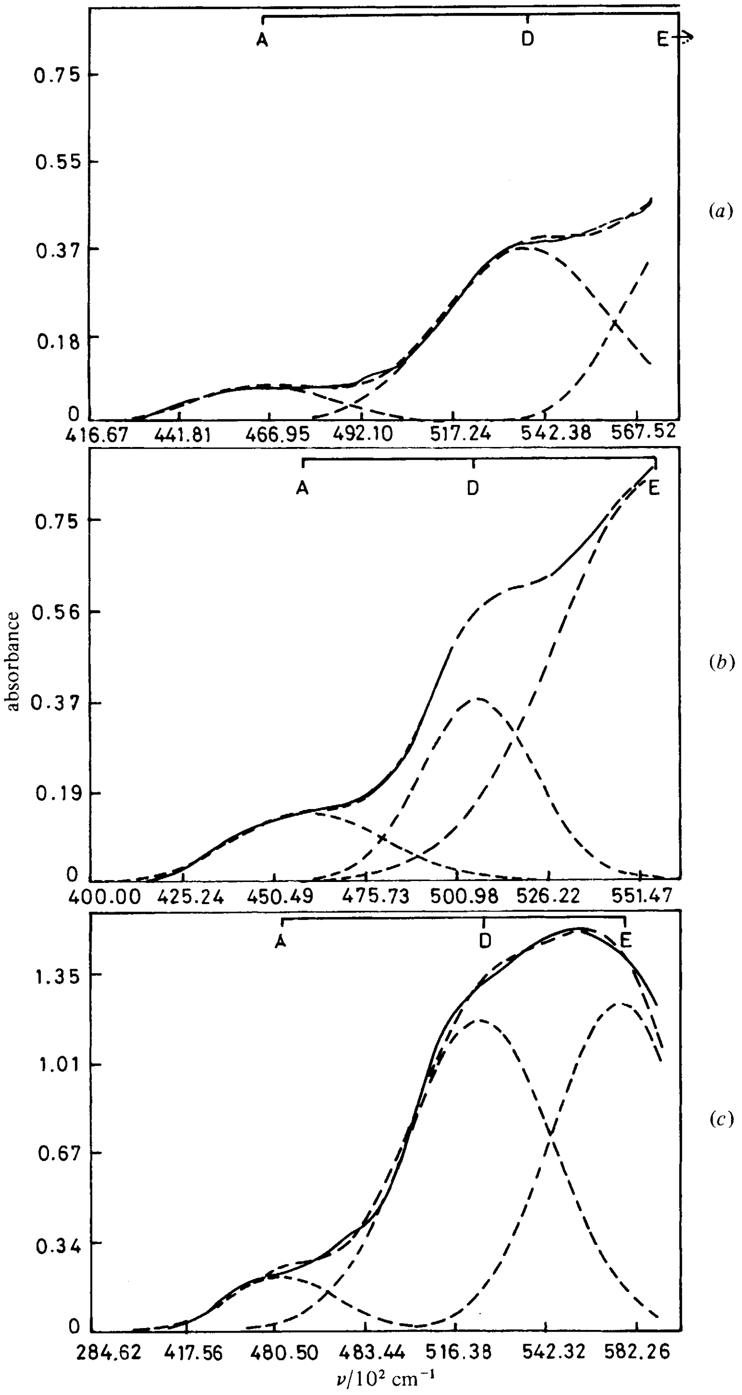

FIG. 1.—Absorption spectra of tetramethylammonium thiocyanate in (*a*) water at 274 K, concentration 5.42×10^{-3} mol dm³; (*b*) propionitrile at 200 K, concentration 5.34×10^{-3} mol dm³; (*c*) triethyl phosphate at 212 K, concentration 6.79×10^{-3} mol dm³. In each case the full line is the experimental spectrum and the broken lines represent the individual-resolved component bands and their summation, as shown.

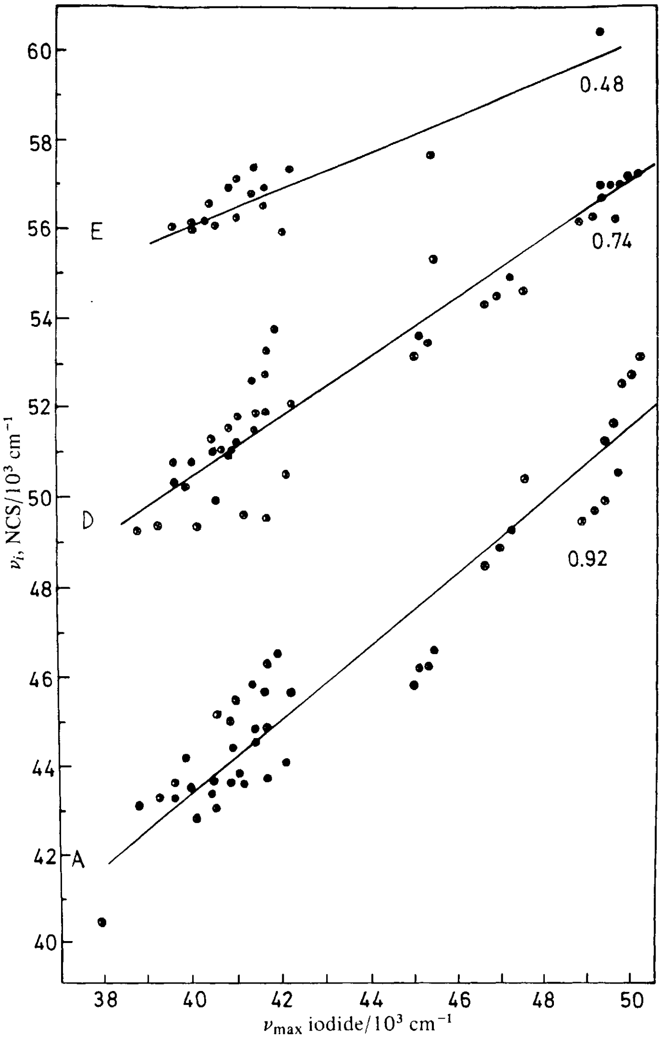

FIG. 2.—Absorption maxima, ν_i, of the resolved A, D and E bands of thiocyanate plotted against ν_{A_1} for iodide in the same combinations of solvents and temperatures. Data for iodide from ref. (4) and ammonia solutions (●) (in the bottom left-hand corner) from ref. (3). Values given for each plot are the best-fitted trend line plots for ν_i (thiocyanate) against ν_{A_1} for iodide.

range of the instrument. Almost all of the blue-shifting solvents show only two bands for thiocyanate, the sole exception being in hexafluoropropan-2-ol at 318 K, where the temperature effect has shifted the entire band system to lower energies.

To develop the solvent sensitivity analysis further, fig. 2 shows the resolved band maxima of the thiocyanate ion absorption spectra for all 48 temperature/solvent combinations plotted against the A_1 iodide maxima under the same conditions.[6] A selection of these results for 298 K is given in table 1. The first band, A, has a solvent sensitivity value relative to iodide of 0.92. This lower value is to be expected if thiocyanate has a larger crystallographic radius than iodide.

TABLE 1.—PARAMETERS OF C.T.T.S. TRANSITIONS FOR THIOCYANATE IN VARIOUS SOLVENTS AT 298 K[a]

solvent	band A			band D			band E		
ammonia[b]	40 500	0.038	2300	—			—		
acetone	43 284	0.094	4838	49 382	0.341	6225	—		
acetonitrile	43 043	0.050	3786	49 811	0.290	6108	56 059	0.89	7300
propionitrile	43 471	0.075	4439	50 791	0.426	6713	56 027	0.528	5604
triethylphosphate	43 601	0.069	4603	51 528	0.667	8093	56 879	0.849	7305
demethoxyethane	45 482	0.100	6062	51 180	0.350	5866	—		
H_2O	46 204	0.104	6152	53 541	0.449	7247	—		
i-butanol	48 865	0.219	7109	54 440	0.913	6022	—		
2,2,2-trifluoroethanol	49 438	0.275	7600	56 100	0.87	7329	—		
1,1,1,3,3,3-hexafluoropropan-2-ol	52 455	0.269	7404	56 980	0.727	6802	—		

[a] Values are given in the order: $\nu_{\max}$, oscillator strength, $\nu_{\frac{1}{2}}$. [b] Values from ref. (3) at 293 K and from inspection of the figures therein.

The solvent sensitivity for band D is reasonably close to that for A (see fig. 2) and has a value relative to iodide of 0.74. The two bands therefore converge and their spacing will slowly vary as $\nu_{\max}$ varies. However, in aqueous solution the splitting is of the order of 7300 cm^{-1}. Band E has an even lower solvent sensitivity value of 0.48 but a similar intensity and half-band width to band D.

The oscillator strengths and half-band widths of bands A and D increase with being shifted to the blue. Thus, band A varies in oscillator strength from a value of 0.053 in acetone at 44981 cm^{-1} to 0.246 at 53083 cm^{-1} in hexafluoropropan-2-ol, whilst ν varies from *ca.* 2300 cm^{-1} in liquid ammonia at 293 K to 6903 cm^{-1} in water at 318 K. Band D shows similar variations for these bands parameters.

The low energy, low intensity band in the region of 30-35000 cm^{-1} was investigated in concentrations up to 0.5 mol dm^{-3} and in cells up to 100 mm path length. In aqueous solutions of potassium, ammonium and tetramethylammonium thiocyanates, the band has a very low intensity, which makes it extremely difficult to separate from the low intensity tail of the 46000 cm^{-1} band. It is clear that the band could not be observed in the other solvents used in this work. The intensity of this band for isolated thiocyanate is very low, less than 0.1 mol dm^3.

DISCUSSION

Discussion of our results has to be taken not only in their own context but also in that of those of McGlynn and coworkers,[1] Treinin and coworkers[3] and Dogliotti and Hayon.[10] Whilst initially in some conflict, detailed examination shows the separate pieces of work to be complementary in thiocyanate ion spectroscopy.

Band A, at *ca.* 46000 cm^{-1} in water, is undoubtedly due to a charge-transfer-to-solvent process and this work only substantiates that conclusion.

The solvent sensitivity of band A is entirely in character with a c.t.t.s. transition of an ion with a slightly larger radius than the iodide ion. The increase in oscillator strength and half-band width for band A with blue-shifted solvents is also consistent with a c.t.t.s. transition. Further evidence comes from the photochemical studies of Dogliotti and Hayon.[10] By the discriminating use of light filters, the two photochemical processes shown to be present were separated into that which occurred below 41 000 cm^{-1} in aqueous solution,

$$NCS^- \xrightarrow{h\nu} CN^- + S$$

whilst that above 41 000 cm^{-1}, associated with the 46 000 cm^{-1} band A, was shown to be:

$$NCS^- \xrightarrow{h\nu} NCS + e^-_{aq}.$$

With the further electrochemical/spectroscopic correlations for the halides and thiocyanate established by Treinin and coworkers,[3] a very complete case for band A to be classified as a charge-transfer-to-solvent process is established.

The establishment of this assignment does not conflict with the work of McGlynn and coworkers.[1] Di Sipio *et al.*[2] point to the forbidden transition in the free ion, which they semi-empirically calculate to occur at 36 800 cm^{-1}, becoming allowed when the thiocyanate is bonded to a metal, as in its transition metal complexes. Close scrutiny of the work of McGlynn[1] shows that the excitation spectra associated with the phosphorescence/fluorescence of the heavy metal solid solutions in water and alcohol at 77 K have maxima at 36 000 cm^{-1}. The emission spectra cannot, therefore, be associated with band A but with the low intensity, forbidden transition centred on 36 000 cm^{-1} which gives rise to the first photochemical process demonstrated by Dogliotti and Hayon.[10] The emission bands shown by McGlynn and coworkers[1] are also cation dependent and show vibrational structure, characteristics not found in c.t.t.s. bands.[5]

Bands D and E have characteristics which are closely analogous to the higher energy band systems observed for the halides and hydrosulphide. Thus, we consider that these bands arise from either higher energy electron transitions, possibly of a *d*-orbital type, or higher states of the thiocyanate radical. Evidence does not exist at present for the spectra of NCS radical in the region above 31 000 cm^{-1}.[14] Further investigation of the NCS radical spectrum is needed to clarify this point.

We conclude that the band system of thiocyanate ion in aqueous solution can therefore be assigned to a very low intensity band at 36 000 cm^{-1}, c.t.t.s. transition bands at 46 600, 55 300 and 57 600 cm^{-1} and the first internal allowed transition predicted by Di Sipio *et al.*[2] occurring at 65 100 cm^{-1}.

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