Spectrum of N3 — in Solution

Itamar Burak and Avner Treinin

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effective field $B(M_A)$ in this coordinate frame is just the vector sum of $A(M_A) - \omega_m$ and $B\gamma_X H_2/2$. One can see from this figure that if $\omega_m = [A(\tfrac{3}{2}) + A(\tfrac{1}{2})]/2$ then $B(M_A)$ will be independent of M_A for the four values $M_A = \tfrac{3}{2}, \tfrac{1}{2}, -\tfrac{1}{2},$ and $-\tfrac{3}{2}$.

Ethyl alcohol has been chosen as an example of a system with two groups of chemically shifted nuclei. Here the spectrum was observed by sweeping the magnetic field while the observing frequency was held fixed at 60 Mc. The spectrum with no irradiation is shown in Fig. 6(a). The irradiation frequency ω_2 was then switched on ($\gamma H_2/2\pi \sim 30$ cps) and the frequency difference $\omega_1 - \omega_2$ was adjusted to give the narrowest CH_2 resonance [see Fig. 6(b)]. The frequency ω_2 was then modulated at 30 cps and the spectrum shown in Fig. 6(c) was obtained. Here a definite narrowing of the CH_2 pattern is noted.

CONCLUSIONS

In double resonance experiments involving loosely coupled systems the perturbing radio frequency field is the most effective when its frequency is equal to the center frequency of the pattern being irradiated. In the usual unmodulated double resonance experiments a complete removal of the residual splittings can be obtained in AX_n systems. In more complex systems the residual splitting is proportional to $(\gamma_X H_2)^{-1}$ in the limit of large perturbing fields, H_2.

By modulating the frequency of the irradiating field at a rate given by Eq. (16), a complete removal of the residual splitting can be achieved in the following additional systems: $A_2X_n, A_3X_n, AKX_n,$ and AK_2X_n. In more complex systems the residual splitting is proportional to $(\gamma_X H_2)^{-3}$ in the limit of large perturbing fields.

Spectrum of N₃⁻ in Solution

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The electronic absorption spectrum of N_3^- in solution was investigated. For this purpose environmental effects on this spectrum were studied, and the thermodynamic properties of the $I_2-N_3^-$ complex were determined. In the 190–300-mμ region the spectrum consists of at least three bands, designated by $A, B,$ and C. Their identification is based on the comparison with the spectra of solid alkali azides. Band A which is of moderate intensity ($\epsilon \sim 400$ liter mole^{-1} cm^{-1}) appears at 230 mμ and is assigned to $^1\Delta_u \leftarrow {}^1\Sigma_g^+$ transition. Band B with λ_{max} at about 200 mμ originates from a charge transfer to the solvent (CTTS). For Band C, the peak of which is at the vacuum uv, a $^1\Sigma_u^+$ excited state is suggested.

The nature of the CTTS state of N_3^- is discussed and evidence is provided for the mixing of this state with the $^1\Delta_u$ state. The investigation of the CTTS band leads to a value for the electron-affinity $E(N_3) = 81$ kcal. One method for deriving this value is based entirely on solvent effects by means of a method which was recently developed. This method yields also an estimate of the crystallographic radius of the ion: $R(N_3^-) \sim 1.92$ Å.

THE absorption spectrum of N_3^- in solution has been the subject of several works, but its description and theory is still far from being satisfactory. Some works treat only the onset of the spectrum,[1,2] while others[3,4] report conflicting descriptions of its short wavelength region. Owing to the close resemblance of N_3^- to the halide ions,[5] its spectrum has been generally attributed to a CTTS process.[2,4] Hardly any experimental work has been performed to support this view and no attempt has been made to detect other electronic transitions

which probably also contribute to the light absorption of this complex ion. Such an analysis should be very helpful for the study of the photochemistry of azides in solution.

The purpose of the present work is to identify the electronic transitions responsible for the uv absorption spectrum of N_3^- in solution. To obtain this two methods were used. (a) Environmental effects on this spectrum were studied in detail, including the effects of temperature, solvent, and added solutes. This method is now of frequent use and has been recently developed to a quantitative solvent scale for the identification of CTTS spectra.[6] (b) The charge-transfer complex of N_3^- with I_2, previously shown to be formed in aqueous solution,[7]

[1] A. Hantzsch, Ber. **66**, 1349 (1933).

[2] J. Weiss, Trans. Faraday Soc. **43**, 119 (1947).

[3] A. Bonnemay and E. T. Verdier, J. Chim. Phys. **41**, 113 (1944).

[4] B. L. Evans, A. D. Yoffe, and P. Gray, Chem. Rev. **59**, 515 (1959).

[5] For a description of this resemblance see, e.g., T. Moeller, *Inorganic Chemistry* (John Wiley & Sons, Inc., New York, 1955), p. 463.

[6] I. Burak and A. Treinin, Trans. Faraday Soc. (to be published).

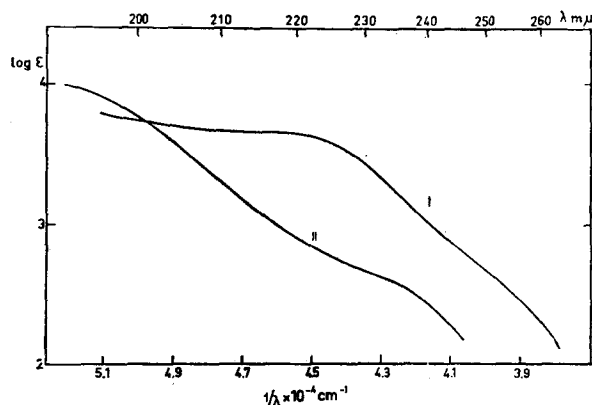[7] D. Meyerstein and A. Treinin, Trans. Faraday Soc. (to be published).

FIG. 1. The absorption spectrum of NaN₃ in H₂O (II) and MeCN (I).

was further investigated and its thermodynamic properties determined. By replacing the solvent as the electron acceptor by I_2, which has a larger electron affinity, the position of the charge-transfer band moves to longer wavelengths and a complete separation from the overlapping bands is possible. This enables us to determine the approximate position of the CTTS band in aqueous solution.

EXPERIMENTAL

Absorption Spectra

Spectrophotometric measurements were carried out with a Hilger Uvispek Spectrophotometer fitted with a high-transmission fused silica prism, using a thermostated cell compartment. During measurements the temperature was kept constant to 0.5°C. Most measurements were carried out at 23°C. Fused silica cells of 10 and 5 mm were used for the region above 210 mμ while, below that, 1-mm cells were employed, the instrument being flushed with nitrogen before measurement. A hydrogen-discharge lamp was the light source. The wavelength calibration was checked with a low-pressure Hg lamp and also with a KI solution, which is known to have two absorption maxima, at 226.2 and 194 mμ at 25°C. Beer's law was satisfactorily obeyed by this solution at 190 mμ, indicating a negligible amount of stray light in the optical region investigated.

Materials and Solutions

Chemically pure NaN₃ was recrystallized from a saturated aqueous solution by adding ethanol. Tetraethylammonium azide was prepared by adding an excess of freshly prepared AgN₃ to a solution of tetraethylammonium iodide in methanol, shaking for 24 h, filtering, and evaporating the filtrate to dryness under vacuum. The azide was then recrystallized from acetone and dried in a vacuum dessicator. This substance was found to be very hygroscopic. Its purity was checked by measuring its spectrum in aqueous solution, which was found to be identical with that of NaN₃.

The solvents used were of purest grade available (methanol and acetonitrile were Kodak Spectrograde), so as to possess high transmission in the optical region investigated. The water was redistilled from alkaline permanganate and then from dilute phosphoric acid in an all-glass still. All other materials used were Analar.

In order to avoid hydrolysis, $10^{-3}M$ phosphate buffer was added to the aqueous azide solution (pH = 7.8). The reference solution used for the spectrophotometric measurements of these buffered solutions contained the same concentration of buffer.

N₃⁻–I₂ Complex

For the investigation of this, complex solutions were prepared containing about $10^{-4}M$ I_2 and between 0.08 and 0.5M NaN₃. The concentration of the aqueous I_2 solution used for preparing the mixtures was determined by adding excess KI and measuring the absorption of I_3^- at 352 mμ, taking $\epsilon_{max} = 26\,400$.[8] The absorption of the complex at 298 mμ was measured in 1-cm cells against a reference solution containing N₃⁻ at the same concentration. The absorption of the free iodine present could be neglected at this wavelength. Measurements were carried out with various azide concentrations at four different temperatures.

RESULTS

Spectrum of N₃⁻, General Features and Temperature Effect

Figure 1 shows the absorption spectrum of N₃⁻ in water and acetonitrile. A shoulder, appearing in water at about 230 mμ, is observed, becoming more distinct as the temperature is lowered (Fig. 2). This is due to the different temperature sensitivities of the two absorption bands which meet at the shoulder: Both bands
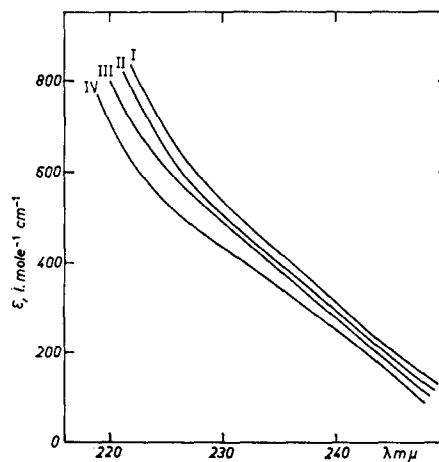

FIG. 2. Temperature effect on the spectrum of $10^{-3}M$ NaN₃; 58°C (I), 43°C (II), 23°C (III), and 8°C (IV).

[8] A. D. Awtrey and R. E. Connick, J. Am. Chem. Soc. 73, 1842 (1951).
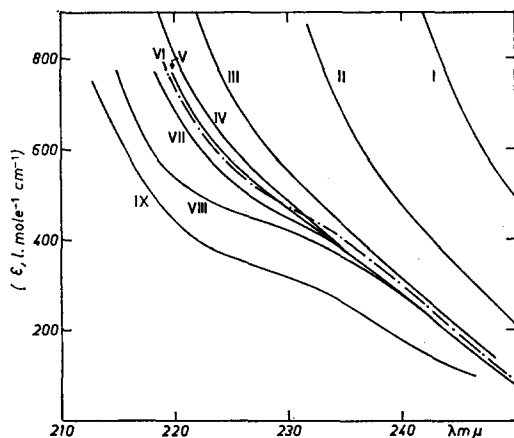
FIG. 3. Solvent effects on the "shoulder" of the spectrum of N₃⁻: (I) MeCN (40-mm cells); (II) MeCN+H₂O (~5%) (NEt₄N₃); (III) 25% NH₃ (1-mm cells); (IV) H₂O; (V) $\frac{1}{2}M$ sucrose (aqueous solution); (VI) methanol; (VII) ethanol; (VIII) ethylene glycol; (IX) 10M KF (aqueous solution). (Unless otherwise stated measurements were carried with 10⁻³M NaN₃ in 1-cm cells.)

FIG. 5. The absorption spectrum of NaN₃ in MeCN+ H₂O mixtures: (I) MeCN at 48°C; (II) MeCN at 23°C; (III) H₂O+99.4% MeCN; (IV) H₂O+98% MeCN; (V) H₂O+88% MeCN; (VI) H₂O+76% MeCN; (VII) H₂O.

are shifted to the red as the temperature is raised, but the temperature sensitivity of the high-energy band (B) is larger than that of the low energy (A). Between $\epsilon=$ 600 and $\epsilon=800$, where the curves are parallel to each other, its temperature coefficients dv_ϵ/dt[9] is about -18 cm⁻¹/deg, i.e., nearly the same as that of the halide ions.[10] On the other hand, dv_ϵ/dt of A (at $\epsilon{\sim}200$) is only about -8 cm⁻¹/deg. This seems to indicate that the shoulder is due to the overlap of two absorption bands of different origins, the high-energy one probably originating from a CTTS transition. Further support to this view is provided by solvent effects.

Solvent Effects

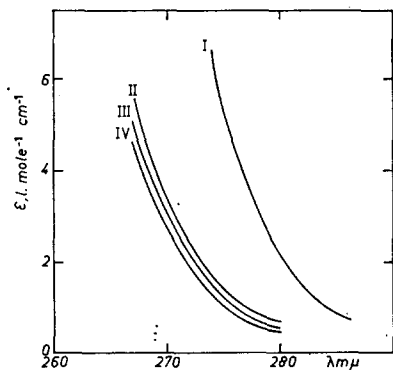Figures 3, 4, and 5 show the spectrum of N₃⁻ in various media. Different types of solvent effects on the

FIG. 4. Solvent effects on band A. 0.1M NEt₄N₃ in: (I) MeCN+H₂O (~5%); (II) methanol; (III) ethanol; (IV) H₂O.

two bands are clearly displayed. Referring to Curves VI, VII, and VIII of Fig. 3, it is of interest to note the opposite effects exerted by the alcohols on the two bands, leading to intersection of absorption curves at the shoulder. (The red shifts exerted by ethanol and glycol on Bands A are very small, so that in Fig. 3 the corresponding parts of the spectra seem to coincide with that of the aqueous solution. In the case of sugar, within experimental error the curves really coincide at $\lambda > 235$ mμ.) In general Band B is more sensitive than A to solvent effects.

The effects on Band B (Fig. 3) resemble very closely those exerted on the halides: the alcohols shifting to uv, with ethylene glycol having the largest effect, while aqueous ammonia and more appreciably acetonitrile shift the band to the red. The close resemblance is further demonstrated in Fig. 6, where we plotted hv of

FIG. 6. $hv(N_3^-)$ at $\epsilon=650$ against hv(max) of I⁻ at the same solvent (i.e., its CTTS value): (1) 10M K F; (2) HOCH₂CH₂OH; (3) C₂H₅OH; (4) CH₃OH; (5) 4M K F; (6) H₂O; (7) H₂O+76% MeCN; (8) H₂O+25% NH₃; (9) H₂O+90% MeCN; (10) H₂O+95% MeCN; (11) H₂O+97.5% MeCN; (12) MeCN.

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[9] Let v_ϵ be the wavenumber at which the extinction coefficient has some chosen value ϵ. Then temp. coef.$=dv_\epsilon/dt$.

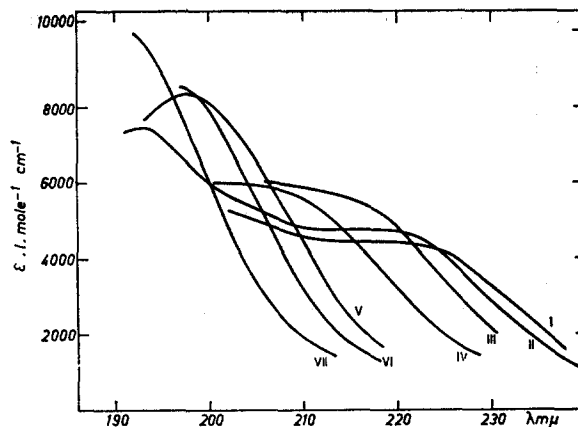[10] G. Stein and A. Treinin, Trans. Faraday Soc. **55**, 1091 (1959).

FIG. 7. The Benesi–Hildebrand plots for I_2–N_3^-: (I) 9.3°C; (II) 15.0°C; (III) 20°C; (IV) 24.0°C.

N_3^- at $\epsilon=650$ against $h\nu_{max}$ of I^- in the same solvent. This ϵ was chosen to lie where the curves are parallel, so as to minimize the interference of the overlapping transitions. The points seem to lie nearly on a straight line, the largest deviation displayed by MeCN. Cl^- and Br^- behave in a similar way, the distinct departure of MeCN being rather expected.[6]

Figure 3 also shows the effect on the region of the shoulder of adding KF and sucrose. Here we notice again that while Band B is appreciably affected by the presence of these solutes, Band A is either weakly affected (KF) or not at all (sucrose). This is a striking example of the "sugar effect" and its use as a tool to distinguish between internal and CTTS transitions.[11]

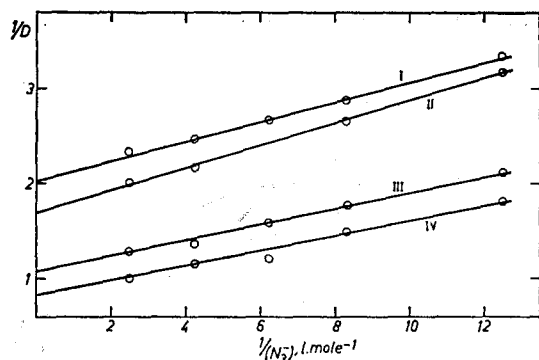In general the effects on Band A (Fig. 4) appear to be of the ordinary "blue shift" type like that exerted on $\pi \leftarrow n$ transitions. But a more detailed examination of the shifts reveal certain features which suggest some kind of "borrowing" from the properties of the CTTS band. Thus though all organic solvents shift the band to the red, the alcohols exert only a small effect while that of acetonitrile is exceptionally large. And among the alcohols, methanol, which is more polar than ethanol, has the largest effect. Since the region studied (270–290 $m\mu$) is quite removed from the shoulder, this "borrowing" does not seem to result from overlapping with the CTTS band.

The absorption spectrum of N_3^- in MeCN (Fig. 5) has a complex pattern. A new band (C) is revealed at the short-wavelength edge of the spectrum. The very broad shoulder extending from 220 to 210 $m\mu$ is rather peculiar. It probably results from the overlap of two bands $(B$ and $C)$ or more. Small concentrations of water bring about an appreciable blue shift of Band B and the gradual disappearance of this shoulder. That no specific interaction of N_3^- with MeCN is taking place could also be ascertained by measuring the spectrum of a very thin film of $1M$ NaN_3 in 25% NH_3 solution. This spectrum, which is not reproduced here owing to the unknown thickness of the film, has nearly

[11] D. Meyerstein and A. Treinin, Trans. Faraday Soc. 57, 2104 (1961).

the same shape and position of peak as that in 76% MeCN+H_2O solution. And indeed these two solvents have close CTTS values.[6]

Complex of N_3^- and I_2

The absorption band of this complex has a maximum at 298 $m\mu$.[7] According to the experimental procedure employed, (see Experimental) the Benesi–Hildebrand relation[12] should take here the following form:

$$1/D = (1/K\epsilon ab) + (1/\epsilon a), \qquad (1)$$

where D is the optical density of the solution, ϵ is the maximum extinction coefficient of the complex, a and b are the total concentrations of I_2 and N_3^-, respectively, and K is the stability constant of the complex. In obtaining Eq. (1), we assume that in the expression of K the activity coefficients ratio is nearly constant at unity.

Figure 7 shows the relation between $1/D$ and $1/b$ at four different temperatures. From the slopes of the straight lines and their intercepts, K and ϵ could be determined. While ϵ is constant, K changes appreciably with temperature. At 24°C, $K=11.4$ mole^{-1} liter, ΔH_f of the complex, obtained by plotting $\log K$ against $1/T$ (Fig. 8) is -6.45 kcal. ϵ_{max} of the complex is 24 000. We could not confirm the last result by determining the absorption of I_2 in a large excess of N_3^- since under these conditions the complex was found to be unstable.

DISCUSSION

Our results indicate that the absorption spectrum of N_3^- in solution between 190–300 $m\mu$ consists of at least three bands, which we denote by A, B, and C.

Band A

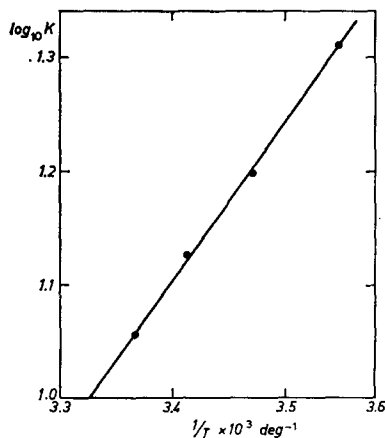Band A is most clearly observed in ethylene glycol and $10M$ KF (Fig. 3). A rough graphical analysis

FIG. 8. The plot of Van't Hoff equation for I_2–N_3^-.

[12] H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc. 71, 2703 (1949).

leads to the following values in glycol: $\lambda_{max}\sim 230$ mμ, $\epsilon_{max}\sim 400$ mμ. Since Band A is only little affected by replacing water by glycol, the band in water probably has almost the same position and intensity.

The spectra of alkali azide crystals exhibit a weak band at about 222.5 mμ with vibrational structure which sharpens at low temperature.[13] This clearly indicates that the band is due to an internal transition. Being an internal transition, its position is not likely to vary appreciably if the N_3^- ion is removed from the crystal and dissolved in water; a shift of no more than 10–15 mμ to the red is expected, as in the case of NO_3^-.[14] When the crystals are irradiated at their weak absorption there is a weak fluorescence at 480 mμ, which means a rather large Stokes shift.[13]

According to its position, Band A seems to be identical with the weak absorption band shown by the crystals. But there is one important difference: though still not strong the intensity of the band in solution is much larger than that displayed by the crystals ($\epsilon = 10-20$[13]). Such an increase of intensity is rather surprising. The weak band of NO_3^- at 300 mμ hardly changes its intensity when crystalline $NaNO_3$ is dissolved.[14] This leads us to suggest that in solution the weak band "borrows" intensity from its neighbor, i.e., that there is some mixing between the excited state corresponding to this transition and the CTTS state. This view is supported by two other pieces of evidence: (a) Solvent effects on Band A suggest some "borrowing" of properties from Band B (see experimental). (b) It was shown[2] and confirmed by some of our preliminary experiments that hydrogen is formed as a result of irradiating an aqueous N_3^- solution by the 2537-Å mercury line, i.e., in the region of the weak band. This suggests a mechanism of electron release to the solvent. A CTTS state does lead to such release, probably after a certain relaxation time necessary for the medium to lose its persistent polarization around the original ion.[14a] Therefore, when as a result of "mixing" the system has once gone to the CTTS state, the electron has the opportunity to "leak" into the solvent. This kind of mechanism resembles a pre-ionization process and its possible occurrence should be taken into account when considering the photochemistry of anions.

The electronic absorption spectra of CO_2, CS_2, etc., the valence shells of which are isoelectronic with N_3^-, show one or two weak bands followed by intense bands at shorter wavelengths.[15] The ground states of these molecules are related to the electronic configurations $(S)^4 (\sigma_g)^2 (\sigma_u)^2 (\pi_u)^4 (\pi_g)^4$. The weak CO_2 band at 1475 Å and the CS_2 band at 3200 Å were assigned by Walsh[16] to the transition $^1\Delta_u B_2 \leftarrow {}^1\Sigma_g^+$. The excited state

involved $^1\Delta_u$ is related to the electronic configuration $\cdots (\pi_g)^3(\bar{\pi}_u)$ (which gives rise to two other singlet states, $^1\Sigma_u^-$ and $^1\Sigma_u^+$). The $^1\Delta_u$ state correlates with two states ($^1B_2$ and $^1A_2$) which are expected to be strongly bent.[17,18] This assignment is now generally accepted. Mulliken previously supposed the $\bar{\sigma}_g$ orbital to lie below the $\bar{\pi}_u$ orbital, thus attributing the long-wavelength absorption to a transition to $^1\Pi_g B_2$ state,[19] but theoretical calculations of the MO energies led him to accept Walsh's view.[18]

We are thus led to assign Band A to $^1\Delta_u B_2 \leftarrow {}^1\Sigma_g^+$ transition. Mulliken's former assignment of the weak band to $^1\Pi_g B_2 \leftarrow {}^1\Sigma_g^+$ makes improbable the mixing of the excited state with the CTTS state, which is of u symmetry (see next paragraph).

Thus the first excited state of N_3^- has its most weakly bound electron in the $a_1' S_A - \bar{\pi}_u$ orbital.[16] The binding energy of this π orbital increases steeply when the angle of the molecule changes from 180° to 90° (see Walsh's correlation diagram).[16] For this reason the first excited state correlates with an equilibrium state which is strongly bent. Therefore when the excited electron returns to the ground state the emitted energy should be much smaller than that necessary for excitation. This explains the large Stokes shift observed.[20] But as Walsh emphasized,[16] a strongly bent excited state by itself does not imply that the $\bar{\pi}_u$ lies below the $\bar{\sigma}_g$ state, since according to the noncrossing rule, the $a_1' S_A$ will be correlated to $\bar{\sigma}_g$ if this orbital should happen to lie below $\bar{\pi}_u$.

The solvent effects displayed by Band A are in accord with its being $\pi \leftarrow n$ type of transition. The π_g orbital is essentially a nonbonding orbital, the electron charge being mainly concentrated on the marginal nitrogen atoms. On the other hand the $\bar{\pi}_u$ orbital is a real antibonding orbital. Therefore, the transition is accompanied by a net flow of negative charge from the marginal nitrogen atoms to the central atom. For this reason the ground state is more liable to H-bond formation than the excited state. Thus it is clear that replacing H_2O by a less polar solvent will cause a shift to lower energies. For the same reason a rise of temperature, which tends to disrupt H bonds, will have a similar effect. Addition of sugar also brings a red shift owing to its desolvating effect (a small red shift was actually observed in several cases: NO_3^-,[11] IO_3^-,[21] etc.). The absence of such an effect may be due to its cancellation by the "borrowed" blue shift from the CTTS band.

[13] S. K. Deb, J. Chem. Phys. **35**, 2122 (1961).

[14] J. A. Friend and L. E. Lyons, J. Chem. Soc. **1959**, 1572.

[14a] J. Jortner, M. Ottolenghi, and G. Stein, J. Phys. Chem. **66**, 2037 (1962).

[15] S. F. Mason, Quart. Rev. (London) **15**, 287 (1961).

[16] A. D. Walsh, J. Chem. Soc. **1953**, 2260.

[17] According to Mulliken, $^1A_2$ is linear but perhaps slightly unsymmetrical.[18]

[18] R. S. Mulliken, Can. J. Chem. **36**, 10 (1958).

[19] R. S. Mulliken, (a) J. Chem. Phys. **3**, 720 (1935); (b) Phys. Rev. **60**, 506 (1941); (c) Rev. Mod. Phys. **14**, 204 (1942).

[20] A large Stokes shift is also displayed by the emission spectrum of CO_2, but in this case the origin of this emission is doubtful.[16]

[21] M. Jakobi and A. Treinin (unpublished results).

I. BURAK AND A. TREININ

Table I. Data concerning series of charge-transfer complexes necessary for the evaluation of $h\nu_{max}(N_3^-)$.[a]

Ion	$h\nu_{max}$ (kcal)	ΔH_f (kcal)	Δ (kcal)[b] (calc.)	$h\nu(N_3^-)$ (kcal) (calc.)
Cl^-	158			
Br^-	147			
I^-	126.5			
OH^-	153			
CNS^-	128			
I_2Cl^-	115	+1.0	42	
I_2Br^-	106	−1.6	42.5	
I_3^-	81.5	−3.6	48.5	
I_2CNS^-	94.5	−8.1	41.5	
$I_2N_3^-$	96	−6.4[f]		134
$Fe^{3+}Cl^-$	91.5	+8.5	58	
$Fe^{3+}Br^-$	76	+6.1	65	
$Fe^{3+}OH^-$	90	−1.2	64	
$Fe^{3+}CNS^-$[c]	64	−1.6	66	
$Fe^{3+}N_3^-$[d]	62.5	−1.5		124
$Co(NH_3)_5Cl^{++}$	104		54	
$Co(NH_3)_5Br^{++}$	91		56	
$Co(NH_3)_5I^{++}$	74.5		52	
$Co(NH_3)_5N_3^{++}$[e]	94.5			148
$Cr(NH_3)_5I^{++}$	98.5		28	
$Cr(NH_3)_5CNS^{++}$[e]	95.5		32.5	
$Cr(NH_3)_5N_3^{++}$[e]	108.5			139

[a] Unless otherwise stated the data for the corresponding ions is taken from: free ions, Refs. 6 and 23; iodine complexes, Ref. (6); Fe^{3+} complexes, M. G. Evans and N. Uri, Symp. Soc. Exptl. Biol. **5**, 130 (1951); halogen complexes of Co^{3+} and Cr^{3+}, M. Linhard and M. Weigel, Z. Anorg. Allgem. Chem. **266**, 49 (1951).

[b] Where ΔH_f is unknown only an approximate value of Δ could be given.

[c] H. S. Frank and R. L. Oswalt, J. Am. Chem. Soc. **69**, 1321 (1947); R. H. Betts and F. S. Dainton, J. Am. Chem. Soc. **75**, 5721 (1953).

[d] R. M. Wallace and E. K. Dukes, J. Phys. Chem. **65**, 2094 (1961).

[e] M. Linhard, H. Siebert, and M. Weigel, Z. Anorg. Allgem. Chem. **278**, 287 (1955).

[f] Present work.

Band B

The onset and peak of this band are overlapped by other transitions. From the spectrum in acetonitrile (Fig. 5), where the band is most apparent, its main features in this solvent could be estimated: $\lambda_{max} = 224$ mμ; $\epsilon_{max} \sim 4000$ mμ. It appears that B is a relatively intense band resulting from an allowed electronic transition. According to its behavior towards environmental effects, which resemble very closely that of the halide ions, we conclude that it originates from a CTTS excitation. Assuming that the shift of the peak, caused by replacing H_2O as a solvent by MeCN, is close to that of the halides (10–15 kcal[6]) it appears

that the peak of N_3^- in aqueous solution should be located at 203 ± 3 mμ. Nearly the same value can be derived from the direct analysis of the spectrum in water. The onset of the CTTS band (at 23°C) derived by extrapolation is at ~235 mμ. The separation between the onset[22] and the peak[23] of Cl^-, Br^-, I^-, OH^-, and SH^- is 22 ± 2 kcal. Assuming that this applies also to N_3^-, it follows that Band B has its peak at 199 ± 3 mμ.

$h\nu_{max}$ of N_3^- in water can be determined also by studying its charge-transfer complexes. Table I reports data on some complexes which exhibit intense absorption bands, presumably due to charge transfer from anion to acceptor. $h\nu_{max}$ of these complexes is related to $h\nu_{max}$ of the anion by the following expression[7]:

$$h\nu_{max}(\text{complex}) = h\nu_{max}(X^-) - \Delta H_f - \Delta, \quad (2)$$

where ΔH_f is the heat of formation of the complex and Δ is essentially a Franck–Condon strain term. Using available data, which are included in the table, Δ could be calculated. It appears that for a given acceptor with different donors Δ is nearly constant. Equation (2) can now be used to estimate $h\nu_{max}(N_3^-)$, by inserting the average value of Δ for a certain group of complexes and $h\nu_{max}$ and ΔH_f (if available) of the corresponding azide complex. The values of $h\nu_{max}(N_3^-)$ thus calculated are recorded in the last column of the table. The agreement is rather poor, indicating that either some of the complexes are not strictly CT complexes or that Δ is not necessarily constant. The value derived from the Fe^{3+} complexes is certainly too low and should be disregarded. Taking the average of the remaining values we obtain $h\nu_{max}(N_3^-) = 140$ kcal, i.e., 204 mμ.

It is of interest to note in the foregoing that Bonnemay and Verdies observed a high intensity peak of N_3^- in aqueous solution at 205 mμ.[3] Though, as we have shown, this may be the real location of the peak of the CTTS band, it could not be observed. Presumably in aqueous solution Band C overlaps the CTTS band in a way that leads the absorption curve to run smoothly.

Now we turn to evaluate the electron affinity of N_3. Three different relations were used for this derivation, two of them based on the value of $h\nu_{max}$ and the third on the solvent effects displayed by the "onset" of the band:

(a) The sum of the heat of solvation $L_{N_3^-}$ and the electron affinity E_{N_3} is related to the transition energy $h\nu_{max}(N_3^-)$ by the following expression:[24]

$$h\nu_{max}(N_3^-) = E_{N_3} + L_{N_3^-} - L_{N_3} - 16 \text{ kcal}, \quad (3)$$

where L_{N_3} is the heat of solvation of the radical. The following values were taken: $h\nu_{max} = 140$ kcal, $L_{N_3^-} =$

[22] L. Farkas and F. S. Klein, J. Chem. Phys. **16**, 886 (1948).
[23] H. L. Friedman, J. Chem. Phys. **21**, 319 (1953).
[24] G. Stein and A. Treinin, Trans. Faraday Soc. **55**, 1086 (1959).

79 kcal.[25-27] L_{N_3} = 5 kcal (assumed to be the same as that of the halogen atoms;[24] an error in this small term will not affect the result appreciably). The value of E_{N_3} thus obtained is 82 kcal.

(b) The transition energy is related to the apparent radius of the ionic cavity in solution r_0 by the expression[24]:

$$h\nu_{max}(X^-) = E_X + (0.77e^2/r_0) - L_X - 1.58, \qquad (4)$$

all values expressed in eV. For many ions it was found that $r_0 \sim 1.25\ r_c$, where r_c is the crystallographic radius of the ion. Taking 2.04 Å as the average crystallographic radius of N_3^-,[25] Eq. (4) yields: E_{N_3} = 81.5 kcal.

(c) The study of solvent effects on the spectra of Cl⁻ and Br⁻ revealed the existence of a linear correlation between $h\nu$ of the halides at constant extinction coefficient ϵ and $h\nu_{max}$ of I⁻ (CTTS value) in the same solvent.[6]

This correlation was given a theoretical interpretation by using the Frank–Platzman picture for CTTS spectra, modified by Stein and Treinin to include the radius of the ionic cavity r_0 as a variable. It was shown[6] that for a given anion X⁻, the intercept of the line I should be related to its slope β_X by the expression

$$I = E_X - \beta_X E_I - B(1 - \beta_X), \qquad (5)$$

where E_X and E_I are the electron affinities of X and iodine, respectively, and B is the binding energy of the electron to the polarized medium in its excited state.

From the parameters of the line in Fig. 6, taking an average value 34 kcal for B[6] the value E_{N_3} = 83 kcal is obtained. From the slope of the line 0.9, the crystallographic radius of N_3^- can be estimated. It was shown[6] that at the same ϵ/ϵ_{max} (ϵ is the molar extinction coefficient) $\beta_X = (R_I^-/R_X^-)\beta_I$, where R_I- and R_X- are the crystallographic radii of I⁻ and X⁻, respectively, β_X and β_I the slopes of their CTTS linear relations. At the onset of the band ($\epsilon \sim 5$) β_I = 0.8. Assuming that β_{N_3} at the onset is the same as at ϵ = 650 (actually it should be a little less[6]) we obtain R_{N_3-} = 1.92 Å. Thus the electron affinity and the crystallographic radius of an anion can be fairly estimated from the mere study of solvent effects on its CTTS spectrum without knowing either its heat of solvation or even its $h\nu_{max}$. Knowing these data one can estimate $h\nu_{max}$ and some important thermodynamic properties of the ion. In the case of N_3^- this completely independent method furnishes support to our estimate of its $h\nu_{max}$.

It should be realized that for polyatomic anions the spectroscopic method leads actually to the vertical ionization potential of X⁻. This is due to the Franck–Condon principle, the radical resulting from the elec-tronic excitation being in the same nuclear configuration as that of the ion. The equilibrium electron affinity should be smaller than the vertical ionization potential by the amount of energy required to bring the nuclei of the radical from their equilibrium configuration to that in the ion. To have an estimate of this packing strain, the following calculation was carried out: assuming that the difference in the N–N bond length between N_3 and N_3^- is the same as in the C–O bond length between CO_2^+ and CO_2,[4] it follows that it is necessary to compress N_3 by Δr = 0.028 Å in order to obtain the strained radical. The force constant corresponding to the symmetrical stretching vibration in N_3 is nearly the same as that for N_3^-,[4] 13.3×10^5 dyn cm⁻¹. The compression energy $\frac{1}{2}k\Delta r^2$ is therefore 0.75 kcal, which is rather a small correction term. We may thus conclude that E_{N_3} = 81 kcal. This is a little larger than the value, E_{N_3} = 69 ± 7, derived from electron impact reported for methyl azide.[4] It appears that in this respect, too, the azide behaves as a pseudohalogen having its place close to Br⁻ (E_{Br} = 81.5). This point is emphasized here because previous calculations, based on the transition energy corresponding to Band A, led to E_{N_3} = 54.[27]

In conclusion, Band B is assigned to electron transfer from the azide ion to the polarized solvent. As far as we know this is the first instance that such a transition is clearly identified as a component of a complex spectrum. Its proximity to other transitions may have pronounced effect both on its own nature and on its neighbors, if the proper selection rules allow mixing of the corresponding excited states. Some evidence to such mixing was presented in the previous paragraph.

The CTTS state of the halide ions probably consists of the halide atom in a P_u state and an electron bound in a $2Sg$ state to the medium.[28] The CTTS transition thus corresponds to an allowed $u \leftarrow g$ transition. The azide radical N_3 is in a Π_g state so that to make the CTTS state of u symmetry, the excited electron should be bound to the medium in a p state, probably $2p$.

The Franck–Platzman model[28] pictures the excited electron as bound in the field of a centrosymmetric Coulomb potential. This should prevail only a relatively large distance from the azide ion. At short distances, the potential of the polarized medium has rather a cylindrical symmetry. Further contributions to this potential will arise from the interaction between the excited electron and the azide radical. Altogether the CTTS state should more closely belong to the (Ω_c, ω) type of coupling, Λ not being defined. The configuration $\pi\pi$ should give rise to four groups of levels, the CTTS being subdivided into four subbands. This may be the reason for its peculiar shape as illustrated in acetonitrile. Complete detachment of the excited electron will bring about only a small doublet splitting due

[25] P. Gray and T. C. Wadington, Proc. Roy. Soc. (London) A235, 481 (1956).

[26] From its lyotropic number L_{N_3}—was estimated to be 71 kcal.[27]

[27] E. H. Buchner, Rec. Trav. Chim. 69, 329 (1950).

[28] R. L. Platzman and J. Franck, Farkas Memorial Volume (Weizmann Press, Jerusalem, 1952), p. 21; Z. Physik 138, 411 (1954).

to the two states of the N_3 radical $^2\Pi_{\frac{3}{2}}$ and $^2\Pi_{\frac{1}{2}}$. This splitting is only 150 cm^{-1}.[29]

However, the properties of Band B indicate that the Franck–Platzman model may still serve as a good first approximation for its interpretation. Thus we have shown that it leads to a plausible value for E_{N_3}. It is of interest to note that the solvent method (Method c) is rather insensitive to the exact value of B, the binding energy of the excited electron.

Band C

The ascending part of this band is clearly detected in the spectrum of N_3^- in acetonitrile. Little can be said on its location and intensity but it appears to be an intense band with its peak falling at the vacuum uv region ($\sim$180 mμ).

Alkali azide crystals exhibit several intense bands in the vacuum uv region.[13] At room temperature two such bands appear: the first at about 190 mμ and the second which is of higher intensity at about 150–160 mμ. The highest energy band splits at very low temperature into two bands, being separated by about 2500 cm^{-1}. Deb assigned the three bands to exciton transitions, the energies of which fit a Rydberg-type relation. In many respects excitons are the crystalline analogs of CTTS states. Thus the first exciton transitions in alkali iodides and bromides have nearly the same energies as the corresponding CTTS bands and they show the regular doublet splitting. But this is not always the rule: crystalline chlorides and fluorides have their first exciton bands far removed from their CTTS bands.

Since the CTTS band of N_3^- is at about 200 mμ, Deb's assignment seems plausible. But then the question arises: where does Band C appear in the spectra of the crystals? Two possibilities should be considered: (a) Band C is overlapped by the first exciton band. But no sign of such overlapping could be detected.[13] Even as a single band it seems rather weak for an exciton band, since the first member of such a series is usually the most intense.[30] (b) The band at 190 mμ is actually Band C, while the first exciton band appears only at about 150–160 mμ. If the last view is valid, then the complex structure exhibited by the high-energy band at low temperatures may be due to the (Ω_c, ω) splitting discussed earlier, though only two subbands appear. The separation of 2500 cm^{-1} may then corre-

spond to the breadth of the shoulder displayed by the spectrum of N_3^- in acetonitrile. On the other hand, the absence of vibrational structure in the 190-mμ band may indicate a fast dissociation process. In conclusion it seems to us that at present no definite identification of the 190-mμ band in crystals can be done.

In solution Band C appears to originate from an intramolecular electronic transition. Its solvent sensitivity is appreciably smaller than that of a CTTS band but still it seems to be largely shifted to the red by replacing H_2O by MeCN (Fig. 5). Walsh identified the intense absorption systems exhibited by some isoelectronic molecules as transitions to $^1\Sigma_u^+$ derived from the $(\pi_g)^3$ $(\bar{\pi}_u)$ configuration.[16] Mulliken rejected this identification for the 1330-mμ absorption system of CO_2,[18] which was found to be rather weak. He suggested instead a transition to a state derived from the electronic configuration $(\pi_u)^3$ $(\bar{\pi}_u)$, i.e., a forbidden $\pi \leftarrow \pi$ transition. But Walsh's assignment may still apply to Band C of N_3^- and to the intense bands exhibited by CS_2, CSe_2,[31] etc.[32] Being essentially a $\pi \leftarrow n$ transition its solvent sensitivity may be close to that of Band A. Being a Σ state it is not liable to mix with the excited state of A which relates to the linear Δ state.[33] On the other hand, mixing between the $^1\Sigma_u^+$ state and the CTTS state may take place.

The spectroscopic study of N_3^- may throw light on its photochemistry and vice versa. The mechanism by which the absorption at the weak band of solid $Ba(N_3)_2$ leads to its photochemistry was recently described.[34] Using radiations which correspond to the different absorption regions may lead to a more definite identification of the electronic transitions involved. Such a research is being carried out.

Note added in proof: After this work was sent for publication a paper was published[35] dealing with the structures and spectra of azide ion and alkyl azides. The identification of Bands A and C, which rests on the basis of molecular orbital theory, agrees with that presented here, but the CTTS band was completely overlooked.

[29] B. A. Thrush, Proc. Roy. Soc. (London) **A235**, 143 (1956).
[30] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

[31] E. Treiber, J. Gierer, J. Rehnström, and K. E. Almin, Acta. Chem. Scand. **11**, 752 (1957).
[32] Mulliken actually suggested that the strong CS_2 bands near 200 mμ are to be identified with such a transition.[19b]
[33] If the 190-mμ band in the crystal is an exciton band, then the reason that A does not appreciably borrow intensity from it is not clear.
[34] P. W. M. Jacobs, F. C. Tompkins, and V. R. Pai Verneker, J. Phys. Chem. **66**, 1113 (1962).
[35] W. D. Closson and H. B. Gray, J. Phys. Chem. **85**, 290 (1963).