Table I. Effect of Pressure on the Position of a ^{81}Br–^{81}Br Line and on the Widths of Some ^{79}Br–^{81}Br Lines (cm^{-1})

	Full-width at half-maximum (cm^{-1})^b					Position (cm^{-1})^c
Pressure	19-1 band			20-1 band		19-1 band
(Torr)^a	$R(35)$	$R(37)$	$P(39)$	$R(62)$	$R(63)$	$R(31)$
0.60	0.028 (4)	0.029 (4)	0.033 (3)	0.031 (4)	0.031 (1)	17,947.921
2.83	0.029 (3)	0.030 (8)	0.034 (3)	0.031 (3)	0.033 (3)	7.913
5.61	0.030 (3)	0.029 (7)	0.035 (3)	0.029 (3)	0.032 (6)	7.915
36.1	0.031 (2)	0.034 (5)	0.037 (3)	0.036 (2)	0.035 (5)	7.914
132	0.054 (2)	0.052 (6)	0.051 (3)	0.051 (2)	0.051 (6)	7.913

^{a} At the temperature of 296°K, the *vapor* pressure of bromine was about 181 Torr. ^{b} Band assignments are in the form $v^* - v$, and line assignments are in the form $R(J)$ or $P(J)$. Each entry is an average of measurements of the number of recordings which appears in the respective parentheses. Lines were chosen because they are not seriously overlapped by their nearest neighbors at any of the pressures; in addition, their quantum numbers are known. The lines are symmetric. ^{c} The line was chosen because it is very close to the ^{84}Kr secondary standard at 5570.2895 Å ($\nu_{vac} = 17947.434$ cm^{-1}). Measurements of three or more recordings of each of two Fabry–Perot orders were averaged for each entry.

have plotted all of the data, and we find the slopes of the lines to be $+0.133$ cm^{-1}/atm and -0.03 cm^{-1}/atm, respectively. The uncertainty in the latter is about 30%. The value 0.133 cm^{-1}/atm for broadening may be refined by plotting the Lorentzian contribution to the width rather than the observed width. This correction increases the result by about 20%, which is within the estimate of error.

Earlier measurements of broadening and shift of emission lines of *atoms* have been made. In those cases, successful interpretation[4,5] has been based on the so-called impact approximation (always valid for half-widths at pressures as low as those of Table I) and on the Lennard-Jones potential energy form

$$V = C_{12}r^{-12} - C_6r^{-6}$$

in which r is the interatomic distance. Since broadening of Br_2 lines does not show dependence on rotational quantum J, the existing theory has been applied here, with

$$V^*(Br_2^*:Br_2) - V(Br_2:Br_2) = \Delta C_{12}r^{-12} - \Delta C_6r^{-6}$$

in which r is now the intermolecular distance and each of the empirical force constants ΔC_{12} and ΔC_6 is the difference between an excited-state value (*) and a ground-state value. Applying the analysis of Hindmarsh, *et al.*,[5] we find $|\Delta C_{12}| = 3000 \times 10^{-104}$ erg cm^{12} and $|\Delta C_6| = 80 \times 10^{-60}$ erg cm^6. It is useful to compare these differences with the values of C_{12} and C_6 for two ground-state Br_2 molecules; from the corresponding-states correlation of Tee, *et al.*,[6] we estimate 640×10^{-104} erg cm^{12} and 1300×10^{-60} erg cm^6, respectively. Thus, the change in C_6 is ~6%.

In rough approximation,[7] ΔC_6 is proportional to $\Delta\alpha$; evidently the ground-state polarizability of Br_2 (6.4×10^{-24} cm^3/molecule) also is changed by only about 6% in this transition. For comparison with a typical valence-shell promotion, we mention the 2600 Å absorption of C_6H_6, in solid solution, for which effects of high electric fields indicate an increase of polarizability of more than 20%.[2]

On account of the rather small effects found for bromine, more extensive measurements on the similar electronic transition of chlorine have been started. Details of work on both molecules will be published elsewhere. If they are feasible, high-field studies of the Br_2 and Cl_2 bands would be of great interest.

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Polarized Electronic Spectra of Tetracyanonickelate(II) at 5°K

Sir:

Ten years have passed since we proposed[1] an interpretation of the aqueous solution electronic absorption spectrum of the square planar (D_{4h}) complex ion, $Ni(CN)_4^{2-}$. Our suggestion that the intense, near-ultraviolet bands be assigned as transitions from occupied d orbitals to the a_{2u} ($4p_z$,π^*CN) virtual orbital in this low-spin d^8 ($^1A_{1g}$ ground state) complex has been largely confirmed by both magnetic circular dichroism (MCD) spectral experiments[2,3] and recent *ab initio* SCF-LCAO-MO calculations.[4] However, there remains a need for absorption band polarization data on optically dilute single crystals, to provide a firm basis for detailed assignments of both the ligand field (LF) and the charge transfer (CT) bands. We have found that suitable crystals can be readily obtained using tetra-*n*-butylammonium as the cation. Here we report the principal results and conclusions of our investigation of the band polarizations of $[(n\text{-}C_4H_9)_4N]_2[Ni(CN)_4]$ at liquid helium temperature.

The σ and π absorption spectra of $Ni(CN)_4^{2-}$ at 5°K obtained from our measurements on single crystals

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(1) H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, **85**, 260 (1963).

(2) P. J. Stephens, A. J. McCaffery, and P. N. Schatz, *Inorg. Chem.*, **7**, 1923 (1968).

(3) S. P. Piepho, P. N. Schatz, and A. J. McCaffery, *J. Amer. Chem. Soc.*, **91**, 5994 (1969).

(4) (a) J. Demuynck, A. Veillard, and G. Vinot, *Chem. Phys. Lett.*, **10**, 522 (1971); (b) J. Demuynck and A. Veillard, *Theor. Chim. Acta*, **28**, 241 (1973).

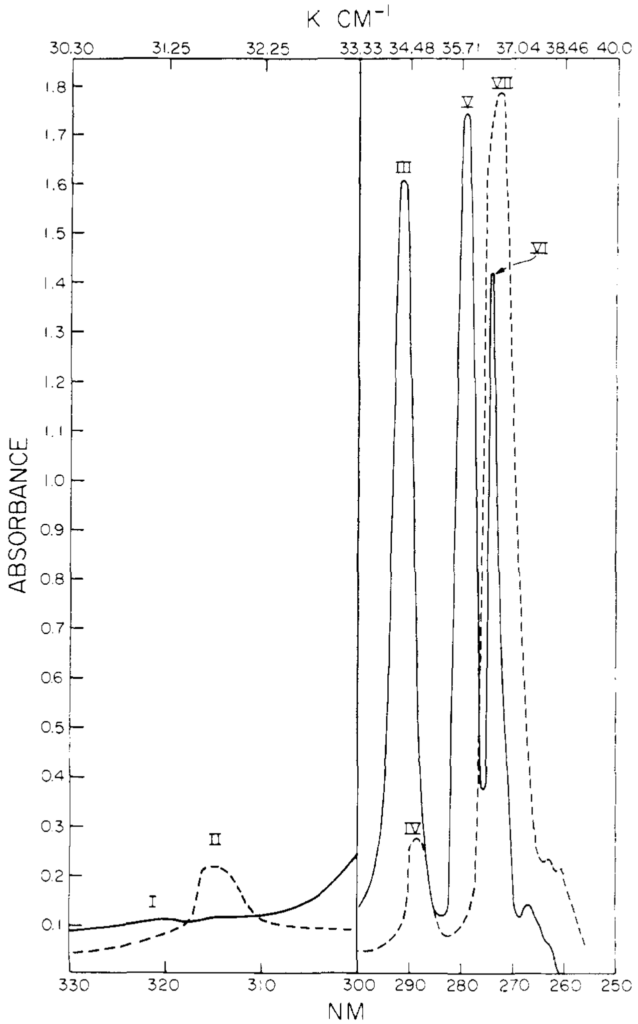

Figure 1. Polarized single-crystal absorption spectra of $[(n\text{-}C_4H_9)_4N]_2[Ni(CN)_4]$ at 5°K: solid line, π spectrum; dashed line, σ spectrum.

of $[(n\text{-}C_4H_9)_4N]_2[Ni(CN)_4]$ are shown in Figure 1.[5] The positions and polarizations of the observed absorption bands are shown in Table I.

The most intense features in the 5°K single-crystal spectra are in good agreement with previously reported 77°K data obtained from frozen EPA solutions of $[(n\text{-}C_4H_9)_4N]_2[Ni(CN)_4]$.[6]

Table I

Band	nm	cm⁻¹	ε (EPA, 77°K)[a]	Pol
I	321.5	31,100	530	π
II	316.0	31,650	840	σ
	(314.0)	(31,850)	Not obsd	σ
III	291.0	34,360	6,200	π
IV	288.5	34,660	Not obsd	σ
V	279.0	35,840	5,200	π
VI	274.0	36,500	Not obsd	π
VII	272.5	36,700	15,200	σ

[a] W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5721 (1968).

First let us consider the three intense bands, III, V, and VII. Originally we assigned[1] bands III and VII to the fully allowed d → a_{2u} CT transitions $^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g} \rightarrow a_{2u}$) and $^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$), respectively. The strong σ polarization of band VII, along with the observation[2,3] of an MCD A term, fully substantiate the $^1A_{1g} \rightarrow {}^1E_u$ assignment. Most interestingly, however, our finding of two intense π-polarized bands can only be understood in terms of allowed transitions to two completely spin-orbit mixed states of A_{2u} symmetry, as first proposed by Piepho, *et al.*,[3] to accommodate the MCD data. Thus, bands III and V are assigned $^1A_{1g} \rightarrow aA_{2u}$ ($^1A_{2u}$,^3E_u) and $^1A_{1g} \rightarrow bA_{2u}$ (^3E_u,$^1A_{2u}$), respectively.

The orbitally forbidden CT transition $^1A_{1g} \rightarrow {}^1B_{2u}$ ($b_{1g} \rightarrow a_{2u}$) has previously been assigned[1] to band II. As the intensity of band II is observed to be temperature independent[6] as well as strongly σ polarized, this assignment must now be rejected. Instead, it is probable that band II arises from one or more of the three spin-allowed LF transitions, $^1A_{1g} \rightarrow {}^1B_{2g}$ ($a_{1g} \rightarrow b_{2g}$), $^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{1g} \rightarrow b_{2g}$), and $^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{2g}$). Cogent arguments have been advanced[7] to the effect that the D_{4h} excited states $^1B_{2g}$ and ^1E_g are unstable with respect to distortion to the D_{2d} states $^1B_2$ and ^1E, respectively. The $^1A_{2g}$ excited state, on the other hand, should be stable in D_{4h} symmetry. Further, semiempirical reasoning places[7] the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in the 30–32-kcm⁻¹ region, and predicts that the energy order of Franck–Condon maxima will be $^1A_{1g} \rightarrow {}^1B_2 < {}^1A_{2g} < {}^1E$. Band II is therefore assigned $^1A_{1g} \rightarrow {}^1E$, as this transition is fully allowed and should be σ polarized. The new assignment of band II is in agreement with the MCD data on $Ni(CN)_4^{2-}$, which show[3] that in aqueous solution there is a transition to a doubly degenerate excited state at about 32.4 kcm⁻¹.

Band I is assigned to the π-polarized $^1A_{1g} \rightarrow {}^1B_2$ transition. Although this band is difficult to locate in the thin-crystal π spectrum (Figure 1), it appears prominently at 31.1 kcm⁻¹ in spectra measured on crystals of $\geq 1\ \mu$ thickness. It is noteworthy that the $^1A_{1g} \rightarrow {}^1B_2$ transition energy is much higher than in inorganic salts containing closely stacked $Ni(CN)_4^{2-}$ planar units. For example, in $Ba[Ni(CN)_4]\cdot 4H_2O$, which features a Ni–Ni distance of 3.36 Å,[8] the π-polarized band attributable to $^1A_{1g} \rightarrow {}^1B_2$ occurs[7] at 23.0 kcm⁻¹. As we have not been able to observe any band maxima below 30 kcm⁻¹ in thick crystals of $[(n\text{-}C_4H_9)_4N]_2[Ni(CN)_4]$, we can only conclude that the $^1A_{1g} \rightarrow {}^1B_2$ transition, which originates in an axial orbital (d_{z^2}), is significantly red-shifted in the inorganic salts by metal–metal interaction. It is also probable that the famous 22.5-kcm⁻¹ band in $Ba[Ni(CN)_4]\cdot 4H_2O$, assigned[9] previously to $^1A_{1g} \rightarrow {}^1A_{2g}$, actually represents a spin-forbidden LF transition enhanced in intensity by the close contact[8] of adjacent Ni(II) atoms in the crystal.

Two relatively weak features remain to be assigned, bands IV and VI. Band VI appears in π polarization and is located 2140 cm⁻¹ higher than band III, sug-

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(5) Crystals of $[(n\text{-}C_4H_9)_4N]_2[Ni(CN)_4]$[6] were grown on aluminum oxide and quartz substrates by evaporation from dichloromethane solution. Spectral data were obtained using a Cary 17 spectrophotometer equipped with an Andonian liquid helium dewar and double Glan-Taylor air-spaced calcite polarizers. Spectra were measured along the extinction directions of the crystals and converted into in-plane (σ) and out-of-plane (π) components. The orientation of the planar $Ni(CN)_4^{2-}$ anions in the crystal was checked independently by polarized infrared spectroscopy, utilizing the σ-polarized E_u mode at 2110 cm⁻¹.

(6) See Table I, footnote *a*.

(7) C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, 4, 514 (1965).

(8) F. F. Larsen, H. R. Bronbaek-Hazell, and S. E. Rasmussen, *Acta Chem. Scand.*, 23, 61 (1969).

(9) J. P. Dahl, R. Dingle, and M. T. Vala, *Acta Chem. Scand.*, 23, 47 (1969).

gesting that it represents one quantum of the a_{1g} $C\equiv N$ stretching vibration (ground-state value = 2141 cm^{-1})[10] built upon the 34,360-cm^{-1} origin of $^1A_{1g} \rightarrow aA_{2u}$. Band IV is logically attributed to a CT transition to a spin-orbit mixed E_u (^3E_u, $^3B_{1u}$, $^3A_{2u}$, ^1E_u) state. Again, our interpretation is in basic agreement with the MCD spectral placement[3] of a doubly degenerate state near 35 kcm^{-1}.

The band shapes generally substantiate the interpretation put forward above and give further insight into the nature of the CT and LF excited states of $Ni(CN)_4^{2-}$. Transitions to the $a_{2u}(4p_z,\pi^*CN)$ orbital should slightly strengthen the Ni—C bonds, while weakening the $C\equiv N$ ones. Excited states derived from the d → a_{2u} transitions should be rigorously planar and not differ significantly in equilibrium internuclear positioning from the ground state, if anything experiencing somewhat reduced Ni-C bond lengths. The fact that the CT transitions give rise to sharp bands, therefore, is in full accord with theory. Of the two LF bands which can be clearly observed, I is unusually broad, as expected from the earlier considerations of the highly distorted nature of the $^1B_2$ excited state.[7]

Our analysis of the electronic spectrum of $Ni(CN)_4^{2-}$ has emphasized the importance of having both low-temperature polarized absorption and MCD spectral data available for assignment purposes. It is highly encouraging that both sets of data fit together as well as they do, providing a consistent interpretation of the main features of the $Ni(CN)_4^{2-}$ spectrum. We will use this interpretation as the foundation for discussion of the liquid helium polarized spectra of $Pt(CN)_4^{2-}$ in a subsequent paper.

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The Unusual Loss of Hydrogen from Ionized 1,5-Hexadiyne

Sir:

Most mass spectral fragmentations occur in times less than 10^{-5}–10^{-6} sec. Thus, mass spectra do not show extensive variations from instrument to instrument, and accurate energetic data can often be obtained with conventional source designs. Unfortunately, access to the time region of prime importance (*i.e.*, less than 10^{-6} sec) can only be gained by special techniques such as field ionization[1] or distinctive apparatus for metastable ion studies.[2] Of considerable interest would be the discovery of a compound which undergoes significant fragmentation in times equal to or *greater* than 10^{-5} sec. Here we wish to report such a compound which undergoes a very slow loss of H. Indeed, this material, 1,5-hexadiyne, is isomeric with benzene, and our results may pertain to questions raised in the copious studies devoted to ionic benzene chemistry.[3]

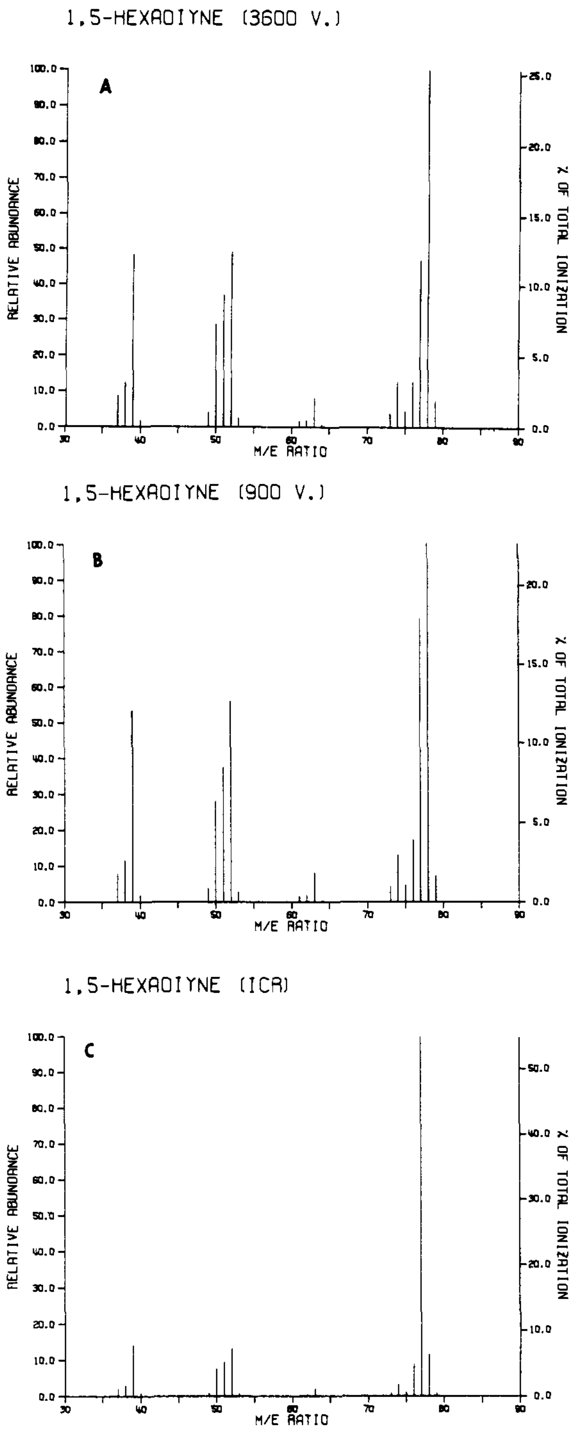

Figure 1. Comparison of mass spectra of 1,5-hexadiyne at various residence times; ionizing energy = 70 eV: (A) from a Hitachi RMU-6D double focusing mass spectrometer, repellers = 7 V; (B) repeller = 1 V; (C) from a Varian ICR-9 spectrometer at 1 × 10^{-7} Torr.

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[2] O. Osberghaus and Ch. Ottinger, *Phys. Lett.*, 16, 121 (1965).

[3] For leading references on various aspects of this work, see H. M. Rosenstock, J. T. Larkins, and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, 11, 309 (1973); T. Keough, T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, 7, 245 (1973); J. H. Beynon, R. M. Caprioli, W. O. Perry, and W. E. Baitinger, *J. Amer. Chem. Soc.*, 94, 6828 (1972).