acetone. Dry. Winnow away any light chaff. *Anal.* Calcd: Br, 64.15. Found: Br, 64.20.

Cs_2OsBr_6. To the hexabromoosmate ion solution above, add a solution of 2.0 g of CsBr in a minimum of HBr. Filter. Wash five times each in absolute ethanol and ether. *Anal.* Calcd: Br, 51.30. Found: Br, 51.50.

K_2PtCl_6. Dissolve 8 g of $H_2PtCl_6 \cdot 6H_2O$ (0.015 mol) in a minimum quantity of warm HCl. Swirl it into a solution of 3 g of KCl in a minimum of HCl. Cool slowly to just below room temperature; filter; wash crystals, while crushing, six times in acetone and four times in ether. *Anal.* Calcd: Cl, 43.78. Found: Cl, 43.58.

Cs_2PtCl_6. Into acidic hexachloroplatinate, as above, stir a solution of 5.0 g of CsCl in 30 ml of HCl. Filter the product. Boil it in 10 volumes of water; filter again; wash five times with acetone and three times with ether. *Anal.* Calcd: Cl, 31.60. Found: Cl, 31.68.

K_2PtBr_6. Boil 5 g of $H_2PtCl_6 \cdot 6H_2O$ for several hours in 250 ml of HBr, reducing the system, at 1 atm, to one-half volume, lowering pressure toward the end to avoid "hotspot" reduction of Pt(IV). Pour this into a solution of 2.5 g of KBr dissolved in a minimum quantity of hot KBr. Cool to 25°; filter; wash five times with acetone and three times with ether. *Anal.* Calcd: Br, 63.65. Found: Br, 63.69.

Cs_2PtBr_6. Into acidic hexabromoplatinate, as above, pour a solution of 4.8 g of CsBr in 25 ml of HBr; filter. Boil the solid in 10 volumes of water; wash, with crushing, in acetone five times and then three times in ether. *Anal.* Calcd: Br, 51.00. Found: Br, 50.60.

A number of samples for which results are reported in Table VII were received from commercial sources, and were purified, where volatile, by repeated sublimations. K_3MoCl_6 was used as received from Climax Molybdenum Co.

B. Nuclear Quadrupole Resonance Apparatus. A self-quenched superregenerative oscillator is operated with feedback provided by connection of the cathode of a triode 6C4 to a center tap on the radiofrequency tank coil. This arrangement affords maximum frequency range for any continuous scan. The coherence level of the oscillator is maintained within the range necessary for maximum signal-to-noise output by comparing the random (incoherence) noise issuing from the oscillator in a narrow band about 500 Hz with a preset norm, and using the deviation from that norm to control a servo-driven potentiometer, which, in turn, provides a variable current to the oscillator's grid. Signal output from the oscillator is obtained by application of a 100-Hz sinusoidal Zeeman magnetic field to the sample, normal to the radiofrequency magnetic field. Phase-sensitive detection is accomplished with a Princeton Applied Research Model HR-8, with integrator time constant operated at 10 sec, with a 12-db/octave rolloff.

Heating and cooling of samples is accomplished using single-pass nitrogen gas systems.

Frequency measurements are made with the use of a Drake Model 2-B communications receiver and crystal converters. During each scan, oscillator carrier and side bands can be monitored. An accuracy of 1 kHz is attainable in favorable cases, *i.e.*, when there are not closely spaced multiple resonances, but normally measurements are made to within ±10 kHz.

C. Vibrational Spectra. Infrared measurements were made with a Beckman IR-11 spectrophotometer, frequency-calibrated using water vapor. The measurements were generally made on Nujol mulls prepared in either a glove bag or an inert atmosphere enclosure. Room-temperature spectra were recorded with the mulls mounted on high-pressure polyethylene sheet. A cryostat was employed to record spectra at liquid nitrogen temperature. High density polyethylene was employed as window material. The sample was mounted on a suitable support at the end of a copper block which was in contact with the liquid N_2 reservoir. CsI, silicon, and polyethylene were employed as low-temperature supports. (The polyethylene is not very useful as a support in low-temperature work because of its poor heat transfer characteristics.)

Raman spectra were recorded on a Perkin-Elmer LR-2 laser Raman spectrometer, fitted with a 4-MW He-Ne source. Standard solid sample mounting techniques were employed.

Electronic and Vibrational Spectroscopy in a Nematic Liquid Crystal Solvent. Band Polarizations for Binuclear Metal Carbonyls

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Abstract: A new technique for obtaining the polarizations of infrared and electronic absorption bands is discussed in detail and illustrated by application to certain binuclear metal carbonyls of the type $M_2(CO)_{10}$. In this method orientation is achieved by dissolving the molecule of interest in a nematic liquid crystal host which is subsequently aligned by a simple rubbing procedure. Infrared polarization data for the binuclear metal carbonyls in nematic solution rigorously establish the assignments of the C≡O stretching bands. The infrared results also determine that the sign of the ordering factor S_{zz}, which describes solute orientation, is positive, indicating parallel alignment of the $M_2(CO)_{10}$ molecules with the nematic host. The degree of orientation obtained by the simple rubbing procedure used in these experiments is comparable to that achieved in liquid crystal nmr experiments. The polarized electronic spectra of $Mn_2(CO)_{10}$ in nematic solution show that the first very intense band is polarized along the metal–metal bond. The band is assigned $d\sigma(M\text{–}M) \rightarrow d\sigma^*(M\text{–}M)$.

Knowledge of polarizations of absorption bands in the ultraviolet, visible, and infrared regions of the spectrum is an invaluable aid in the elucidation of transition assignments. Numerous methods exist to determine band polarizations; among them are single-crystal techniques (both absorption[1] and reflection[2]), photoselection,[3] stretched films,[4] and cholesteric-liquid-crys-

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[1] D. S. McClure, *Solid State Phys.*, **8**, 1 (1959); **9**, 399 (1959); H. C. Wolf, *ibid.*, **9**, 1 (1959).

[2] B. G. Anex, *Mol. Cryst.*, **1**, 1 (1966).

tal[5] methods. For a variety of reasons, however, each of these techniques is often not generally applicable.

Recently, we have reported in preliminary communications[6,7] that the use of nematic liquid crystal solvents[8,9] offers certain advantages in band polarization studies. The basic idea is that molecules in the nematic state behave as a uniaxial crystal in the presence of some external constraint. A solute dissolved in such a host experiences an anisotropic environment and also becomes oriented. The present paper describes in detail the application of this method in electronic and vibrational spectral studies of certain binuclear metal carbonyls and discusses the relative merits of the technique.

Experimental Section

Materials. Butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenylcarbonate (BPC) was obtained from Eastman Organic Chemicals. The compound was recrystallized from methanol before use. On warming, BPC becomes nematic at ~56° and isotropic at ~87°; it is possible to supercool nematic BPC to 40° for a period of several hours. The properties of BPC as a solvent have not been fully investigated, but it is clear that most ionic materials are not sufficiently soluble to allow spectroscopic investigations of the type presented in this paper.

The compounds $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from Pressure Chemical Co. The mixed dimer, $MnRe(CO)_{10}$, was generously provided by Dr. J. M. Smith. A sample of $Mo(CO)_6$ was obtained from the Climax Molybdenum Corp. These materials were purified by sublimation immediately prior to use. Reagent grade benzonitrile was used.

Sample Preparation and Spectral Measurements. Polarized infrared studies of pure nematic liquid crystals[10] demonstrate that the rubbing procedure first used by Chatelain[11] is effective for uniformly orienting nematic solvents. Our modification of this technique is described as follows. One side of each of two BaF_2 windows was rubbed approximately 125 times in one direction with a paper tissue. A camel's hair brush was also found to be effective. A short path length Teflon spacer of 0.025-mm thickness was placed on one of the windows on the side that had been rubbed. The windows together with the rest of an infrared demountable cell assembly were placed in an oven at ~90°. Solutions were prepared by dissolving 0.5–2.0 mg of powdered solute in ~100 mg of BPC. This mixture was placed in the same oven. After 15 min, by which time the solution was homogeneous and isotropic, a few drops of the liquid solution were pipetted into the window with the spacer. The other window was fixed in place, making sure that the rubbed surface was facing inward with its direction of rubbing the same as that of the other window. The assembled cell was placed in the cell compartment, and after allowing a few minutes for temperature equilibrium, the spectra were recorded. The solution at this stage was in the nematic phase. Infrared spectra were taken on a Perkin-Elmer Model 225 infrared spectrophotometer equipped with a common beam, wire-grid polarizer accessory with a double mount for polarization studies from 4000 to 200 cm^{-1}. The heat generated by the source of this instrument maintained the cell compartment temperature at 40° and allowed ample time for the experiment before the BPC solvent solidified. Nothing was placed in the reference beam.

Because of the sensitivity of BaF_2 plates to thermal shock, it is important to allow them to cool to room temperature (after their removal from the spectrophotometer and separation from each other) before cleaning with a solvent. Plates of BaF_2 were chosen instead of KBr in the 2000-cm^{-1} region, where most of the work was done, because of their higher resistance to damage from scratching and handling.

The visible spectral experiments were performed in the same manner, except that quartz plates and a short path length uv cell assembly (from Beckman Instruments, Inc.) were used. Visible and near-ultraviolet spectra were recorded on a Cary Model 14 CMRI spectrophotometer equipped with polarizing filters in the sample and reference compartments; the cell compartment was thermostated at ~56°. Path lengths up to 0.2 mm have been successfully employed for work in the visible region. In all cases, the base line for the BPC was recorded and found to be highly reproducible.

Temperature control does play a role in this experimental technique. No changes were observed in visible spectra over several hours because of the thermostated cell compartment. However, in the infrared spectra, after about 1 hr, changes began to be noticed due to cooling and solidifying of the sample. Thermostating the infrared cell compartment would be advantageous. Attention must also be paid to the amount of solute. If solutions are too concentrated, the solute itself may form a precipitate.

Theoretical Section

Molecules dissolved in an oriented nematic phase are not rigidly fixed but, rather, enjoy a degree of mobility intermediate between that of the liquid and solid. As a result, molecular properties measured in the nematic phase are an *anisotropic* average over many molecules. Thus, to interpret the dichroism observed in these experiments, it is necessary to derive a relationship between the observed polarization data and the absorbances along molecule-fixed axes.

For this purpose, the results of Saupe[12] provide a convenient starting point. Saupe showed that the average value of the diagonal components of any second-rank tensor in the laboratory fixed axis system, $\langle T_{\alpha\alpha}\rangle$, can be related to its components T_{kl} in a molecular framework in the following way.

$$\langle T_{\alpha\alpha}\rangle = {}^1/_3\sum_{k=1}^{3} T_{kk} + (\cos^2\varphi_\alpha - {}^1/_3)\sum_{k,l} S_{kl}T_{kl} \qquad (1)$$

In eq 1 φ_α is the angle which the external orienting constraint makes with the α axis in the laboratory. S_{kl}, the ordering matrix, is defined as follows.

$$S_{kl} = \left\langle \frac{3\cos\theta_k\cos\theta_l - \delta_{kl}}{2} \right\rangle$$

Here θ_k represents the angle which the kth axis in the molecule makes with the optic axis of the liquid crystal. The brackets represent a time or ensemble average of the angular function.

For parallel orientation of the kth molecular axis, S_{kk} is positive with a maximum value of +1. Perpendicular alignment is indicated by negative S values which may extend to a limit of $-{}^1/_2$. Clearly, $S_{kl} = 0$ for isotropic phases where there is no order. This is also true for spherically symmetrical solutes in a nematic solvent since no single orientation will be favored over others.

Since absorption intensity depends on the square of the transition dipole components, eq 1 can be used in the interpretation of our experimental results. For ab-

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(3) A. C. Albrecht, *J. Mol. Spectrosc.*, **6**, 84 (1964).

(4) E. W. Thulstrap and J. H. Eggers, *Chem. Phys. Lett.*, **1**, 690 (1968).

(5) E. Sackmann, *J. Amer. Chem. Soc.*, **90**, 3569 (1968).

(6) G. P. Ceasar and H. B. Gray, *ibid.*, **91**, 191 (1969).

(7) G. P. Ceasar, R. A. Levenson, and H. B. Gray, *ibid.*, **91**, 772 (1969).

(8) For a detailed discussion of the properties of the nematic state see G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, Inc., New York, N. Y., 1962.

(9) For a recent review of liquid crystal work, see A. Saupe, *Angew. Chem., Int. Ed. Engl.*, **7**, 97 (1968).

(10) W. Maier and G. Englert, *Z. Elektrochem.*, **64**, 689 (1960).

(11) P. Chatelain, *C. R. Acad. Sci., Paris*, **213**, 875 (1941).

(12) A. Saupe, *Z. Naturforsch., A*, **19**, 161 (1964).

sorption spectra taken with the electric vector parallel to the direction of rubbing, the absorbance is given by

$$A_{\|} = \frac{1}{3}(A_x + A_y + A_z) + \frac{2}{3}(S_{xx}A_x + S_{yy}A_y + S_{zz}A_z)$$

while for the perpendicular case

$$A_{\perp} = \frac{1}{3}(A_x + A_y + A_z) - \frac{1}{3}(S_{xx}A_x + S_{yy}A_y + S_{zz}A_z)$$

Subtraction of these two expressions yields the important relationship between the dichroism observed, $A_{\|} - A_{\perp}$, and the absorbances along molecule-fixed axes

$$A_{\|} - A_{\perp} = S_{xx}A_x + S_{yy}A_y + S_{zz}A_z \qquad (2)$$

The absorbances defined relative to molecular coordinates A_x, A_y, and A_z are important because it is these quantities which yield information about the symmetries of the states involved in the absorption transition.

For molecules with a threefold or higher axis of symmetry, $S_{xx} = S_{yy} = -{}^1/_2S_{zz}$ and eq 2 then simplifies to

$$A_{\|} - A_{\perp} = S_{zz}(A_z - A_{x,y}) \qquad (3)$$

Clearly, for axially symmetric molecules only the orientation of one molecular axis, the symmetry axis, need be known to specify completely the orientation of the solute.

By rearranging eq 3, it is possible to express S_{zz} in terms of the dichroic ratio $R = A_{\|}/A_{\perp}$. To derive this relationship, it should be noted that $A_z - A_x$ is proportional to $\mu_z^2 - \mu_x^2$ where μ_i is the transition dipole moment in the ith direction. Then

$$\begin{aligned} \mu_z^2 - \mu_x^2 &= \mu_z^2 - \frac{1}{2}(\mu_x^2 + \mu_y^2) \\ &= \mu^2\left(\cos^2\varphi - \frac{1}{2}\sin^2\varphi\right) \\ &= \mu^2(3\cos^2\varphi - 1)/2 \end{aligned}$$

where φ is the angle which the transition dipole moment vector for a particular absorption makes with the z axis of symmetry. We then have

$$A_z - A_x = (A_x + A_y + A_z)(3\cos^2\varphi - 1)/2$$

Since μ^2 is invariant to the choice of axes, $\mu^2 = \mu_{\|}^2 + 2\mu_{\perp}^2$ in the laboratory system. Thus, $\mu^2 \propto A_x + A_y + A_z = A_{\|} + 2A_{\perp}$. By using these results with eq 3, the desired expression is obtained.

$$S_{zz} = \frac{R-1}{R+2}\frac{1}{\frac{1}{2}(3\cos^2\varphi - 1)} \qquad (4)$$

Therefore, if the polarization of the band of interest is independently known, it is possible to determine explicitly both the sign and magnitude of S_{zz} using eq 4.

Polarized electronic spectroscopy[6] and nmr experiments[13] indicate that, in general, solute molecules orient with a long axis parallel to the alignment of the liquid crystal molecules. As we shall demonstrate here, the orientation may also be found in favorable cases from the polarized infrared spectra of molecules dissolved in nematic solution.

Results and Discussion

Spectra of BPC. The polarized infrared and visible spectra of BPC are shown in Figures 1 and 2, respectively. It is important to note that *parallel* (‖) *and perpendicular* (⊥) *are designated with respect to the direction of rubbing.* Previous work[10,11] has shown that the long axes of nematic molecules line up parallel to the direction of rubbing. This is also evident from the polarized infrared spectra of BPC. The two bands between 1700 and 1800 cm^{-1} are attributed to C=O stretching, for which transitions should occur only if the electric vector of light is parallel to the bond axis and hence perpendicular to the long axis of the BPC molecule. The bands at 1600 cm^{-1} are due to C=C stretching in the aromatic rings; such stretches will be of far greater intensity parallel to the long axis of BPC than perpendicular to it. Since the 1600-cm^{-1} bands are polarized parallel to the direction of rubbing and the C=O stretching bands are perpendicular, clearly BPC has oriented parallel to the direction of rubbing.

The infrared spectra of BPC show that it will be useful as a transparent host solvent from 1800 to 2800 cm^{-1}. Also, there are no absorptions in the range 3100–30,000 cm^{-1}. (The near-ultraviolet range may be extended somewhat by the use of very short path length cells or by placing a BPC sample in the reference compartment.) The region 200–450 cm^{-1} is relatively clear and should be useful (the region below 200 cm^{-1} has not been investigated). For examination of the lower energy regions, KBr and polyethylene windows were used; the direction of orientation of BPC on these surfaces was found to be the same as that on BaF_2.

From the most intense band at 1600 cm^{-1}, we can calculate S using eq 4 with $\varphi = 0°$. The value obtained is ~0.5 for the case when no spacer is used (*i.e.*, the two plates are just pressed together). Since the main purpose of this study is to determine directions of orientations and band polarizations, we have not made a substantial effort to determine S values with a high degree of accuracy. The value obtained is within the range reported by other workers for the pure nematic phase using both infrared[10] and nmr techniques.[9,13]

Infrared Spectroscopy. Liquid crystal spectroscopy in the infrared region is very useful not only in helping to assign the bands but also in determining the orientation of the solute molecules relative to the laboratory coordinate (direction of rubbing). The infrared spectra of dimanganese decacarbonyl and related complexes nicely illustrate these points. The $M_2(CO)_{10}$ molecules under consideration have D_{4d} symmetry; this structure consists of two tetragonal pyramidal $M(CO)_5$ units joined at the bases by a metal-metal bond.[14,15] Group

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[13] For a review of nmr spectroscopy in liquid crystals see A. D. Buckingham and K. A. McLauchlan, *Progr. Nucl. Mag. Resonance Spectrosc.*, 2, 63 (1967).

[14] L. F. Dahl, E. Ishishi, and R. E. Rundle, Jr., *J. Chem. Phys.*, 26, 1750 (1947).

[15] L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, 16, 419 (1963).

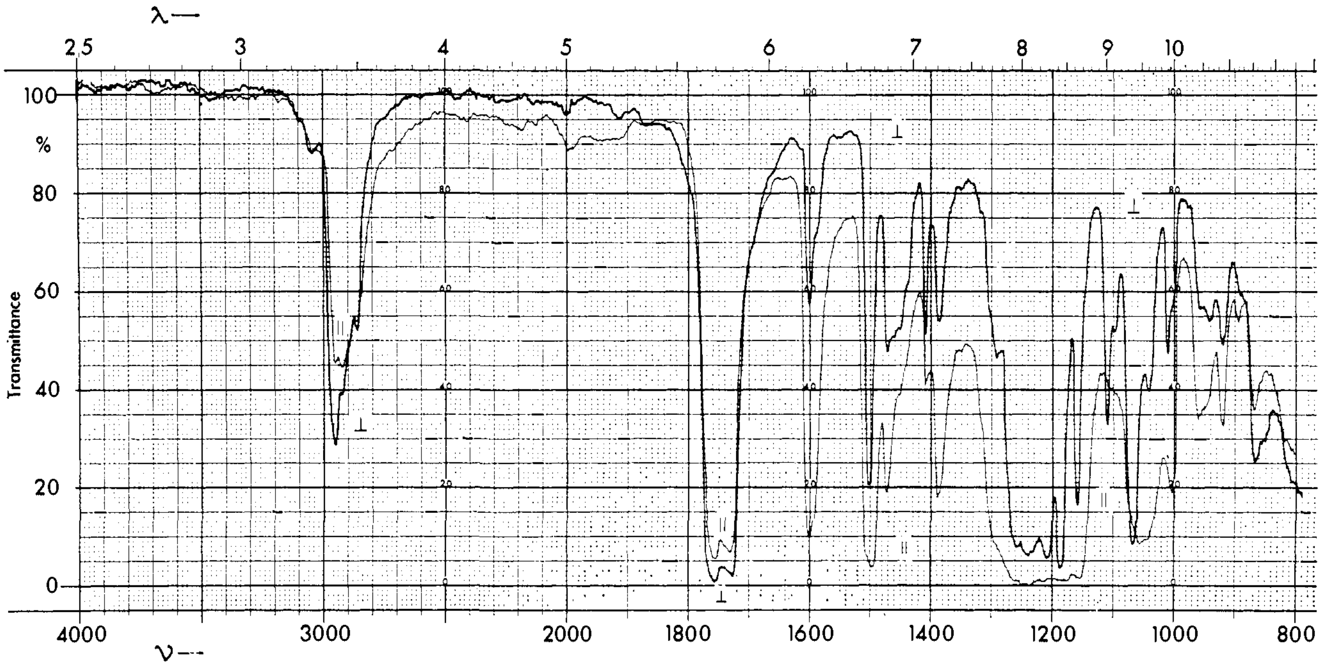

Figure 1. Polarized infrared spectra of butyl *p*-(*p*-ethoxyphenoxycarbonyl)phenylcarbonate in a "super cooled" nematic state at ambient temperature. The spectra are for the electric vector of light polarized || and ⊥ to the long axis of the molecule.

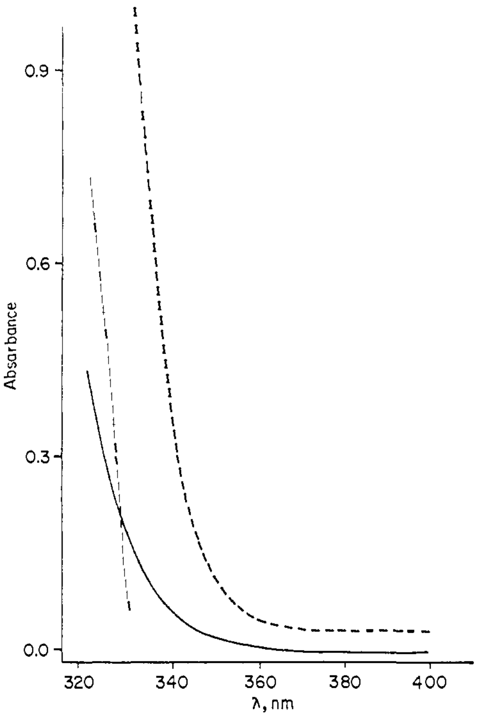

Figure 2. Polarized near-ultraviolet spectra of BPC. The path length is 0.025 mm. The spectra are for the electric vector of light polarized || (- - - -) and ⊥(———) to the long axis of the molecule.

theory predicts three infrared active C≡O stretching fundamentals. Two are of B_2 symmetry and are *z* polarized, where *z* is along the metal–metal axis of the molecule, and the other is of E_1 symmetry and is *x*, *y* polarized.

Polarized infrared spectral data for $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$ in the region 2100–1900 cm^{-1} are given in Table I. The fact that in each of the $M_2(CO)_{10}$ complexes the two outside bands are of different polarization than the middle one immediately pinpoints them as the B_2 fundamentals; thus the more intense middle band is the E_1 mode. These results verify an interpretation of the $M_2(CO)_{10}$ spectra proposed by Flitcroft, Huggins, and Kaesz[16] on the basis of force constant calculations and intensities. The mixed-metal dimer has C_{4v} rather than D_{4d} symmetry; however, the polarizations found here are consistent with assignments previously made,[16,17] regardless of whether or not coupling is assumed across the metal–metal bond.

Table I. Polarized Infrared Absorption Data for Decacarbonyldimetal(0) Complexes in Nematic BPC

		Band[a]		
Complex		aB_2	E_1	bB_2
$Mn_2(CO)_{10}$	$\bar{\nu}$, cm^{-1}	2045	2009	1980
	$A_{\parallel}$	0.62	0.81	0.21
	$A_{\perp}$	0.54	0.92	0.19
$Re_2(CO)_{10}$	$\bar{\nu}$, cm^{-1}	2070	2010	1967
	$A_{\parallel}$	0.47	1.03	0.33
	$A_{\perp}$	0.39	1.16	0.25
$MnRe(CO)_{10}$	$\bar{\nu}$, cm^{-1}	2054	2013	1970
	$A_{\parallel}$	0.47	0.78	0.30
	$A_{\perp}$	0.40	0.93	0.26

[a] Band positions differ slightly from those of ref 16 because of the different solvent medium employed. Absorbance is given in arbitrary units. The spectra have been corrected for background absorption by the nematic solvent.

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(16) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 3, 1123 (1964).

(17) F. A. Cotton and R. M. Wing, *ibid.*, 4, 1328 (1965).

Since the z-polarized B_2 bands are more intense parallel to the direction of rubbing, the long axes of the $M_2(CO)_{10}$ molecules must be oriented in the direction of rubbing and thus parallel to the alignment of the BPC molecules. Hence, S_{zz} has a positive value. The same result is obtained from eq 4, since $\varphi = 0°$ for the B_2 bands. The observed orientations agree with the basic assumption that the long axes of the $M_2(CO)_{10}$ molecules should align with the long axis of the BPC. For $Mn_2(CO)_{10}$, the distance across the z axis is 1.5 times that across the shorter x and y axes.[14,15] Calculated S_{zz} values for these molecules using the most intense (E_1) band are all approximately 0.1 for a path length of 0.025 mm.[18] Again, no attempt was made to determine these numbers precisely; however, the direction of orientation has been rigorously established as have the band assignments. A value of 0.1 for S_{zz} is similar to values obtained for oriented solutes as determined by the nmr technique.[9,13]

In the infrared region, the number of bands determines the amount of information that can be obtained. If one band is measured, the orientation of the molecule can be determined. For the C≡N stretch of benzonitrile, $A_{\parallel} - A_{\perp} = 0.05$, indicating orientation of the cyano group parallel to the direction of rubbing. Information concerning orientation extracted from such infrared experiments will be useful in nmr liquid crystal studies, where often the absolute signs of spin–spin coupling constants remain uncertain because the orientation of the molecule under investigation is not known.[13] Note that introduction of a -CN group into most organic compounds should allow the orientation to be determined. This is conveniently accomplished if BPC is used as the nematic solvent, because BPC is clear in the C≡N stretching region. The situation is optimal when three bands are observable, with one band uniquely polarized, as in the $M_2(CO)_{10}$ system just discussed. For this case both orientation and band assignments can be unambiguously determined.

Visible and Near-Ultraviolet Spectroscopy. Figure 3 shows the polarized electronic spectra of $Mn_2(CO)_{10}$ in the region of the first intense ($\epsilon \sim 2 \times 10^4$) absorption band. Since the infrared work has established that the long axes of the $Mn_2(CO)_{10}$ molecules are oriented parallel to the direction of rubbing, the electronic band (band II) at 29,400 cm^{-1} is polarized along the metal–metal (z) axis. The polarization of the weak shoulder (band I) on the low energy side of this band is not clear because of the large degree of overlap with the major band. Polarized spectra of the other decacarbonyls are not reported since the band maxima of these compounds are at somewhat higher energies and thus out of the range of the BPC solvent (see Figure 2).

An assignment of the z-polarized band is possible after consideration of recent work on the electronic spectra of certain mononuclear metal carbonyl complexes. The neutral hexacarbonyl $Cr(CO)_6$ has its first intense band at 35,700 cm^{-1}; this band has been assigned to the lowest allowed M → L charge-transfer transition.[19] For comparison, the lowest such charge-transfer band in $Fe(CO)_5$ is reported to be at 41,000 cm^{-1}.[20] It is generally the case that the energy of M → L charge-transfer transitions increases with atomic number in an analogous series of complexes because of the increase in the stability of the metal orbitals from which the excitation originates. This point is clearly demonstrated in the $M(CN)_6{}^{3-}$ series in which the energy of the first charge-transfer band increases from 38,600 cm^{-1} in $Cr(CN)_6{}^{3-}$ to 50,000 cm^{-1} in $Co(CN)_6{}^{3-}$.[21] Even allowing for the difference in structure in the series $Cr(CO)_6$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$, it is very likely that the first M → L band in $Mn_2(CO)_{10}$ will fall between 36,000 and 41,000 cm^{-1}. Band II in $Mn_2(CO)_{10}$ is observed at 29,400 cm^{-1}, some 8000 cm^{-1} lower in energy than would be expected for a M → L excitation. The formation of a metal–metal bond does not provide any mechanism for such a large lowering in the transition energy; if anything, the effect of the metal–metal bond would be in the opposite direction. The $d\pi$ (*i.e.*, d_{xz}, d_{yz}, d_{xy}) orbitals should be lower in energy than in $Cr(CO)_6$ on the basis of the larger atomic number of Mn; the interaction between the $d\pi$ orbitals on the two metal atoms should be small.[22] On the basis of these arguments, we rule out a $d\pi \rightarrow L$ transition as a possible assignment for band II. There then remains the metal–metal bond itself. We shall denote $d\sigma$ as the molecular orbital which corresponds to the metal–metal bond; it has the form $[d_{z^2A} + d_{z^2B}]$ (where A and B refer to the two metal atoms) and is of a_1 symmetry in the point group D_{4d}. The corresponding antibonding orbital $d\sigma^*$ is of b_2 symmetry. It is difficult to place $d\sigma$ relative to the $d\pi$ levels; bond formation will tend to position it lower, whereas the interaction with

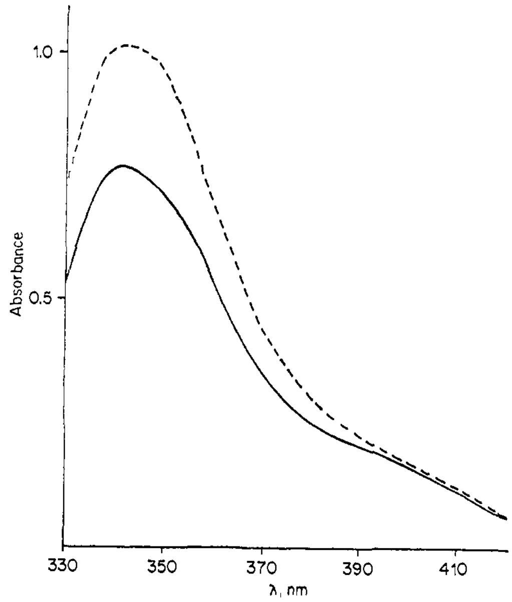

Figure 3. Polarized spectra of $Mn_2(CO)_{10}$ dissolved in BPC; the spectra are corrected for the absorption of BPC. The path length is 0.025 mm. The spectra are for the electric vector of light polarized ∥ (- - - -) and ⊥ (———) to the long axis of the molecule.

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[18] We note here that we have measured $(A_{\parallel} - A_{\perp})$ for the 1981-cm^{-1} band in the octahedral molecule $Mo(CO)_6$; the value is zero, as required by symmetry.

[19] N. A. Beach and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 5713 (1968).

[20] M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, submitted for publication.

[21] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, 90, 4260 (1968).

[22] A semiempirical molecular orbital calculation places all 12 $d\pi$ electrons within 3000 cm^{-1} of each other and at approximately the same energy as the t_{2g} set in $Cr(CO)_6$: R. A. Levenson, unpublished results.

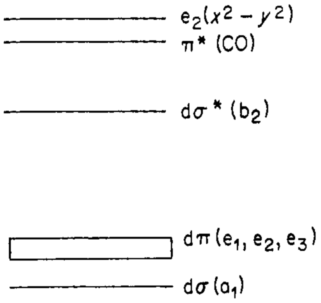

Figure 4. Suggested relative energies for selected spectroscopically important molecular orbitals for $Mn_2(CO)_{10}$. The level labeled π^*(CO) refers to the lowest antibonding π molecular orbital level associated primarily with the carbonyl groups.

the terminal CO groups will tend to raise it. As we noted earlier, however, it is not reasonable to place the $d\sigma$ orbital much above the $d\pi$ levels. Therefore, we rule out the possibility of $d\sigma \rightarrow L$ as the assignment of band II.

The only likely candidates for band II are the allowed transitions between different orbitals associated with the metal–metal bonding. These transitions will be discussed in relation to a qualitative molecular orbital scheme for $Mn_2(CO)_{10}$, which is presented in Figure 4. It is realized that the three $d\pi$ levels will be at somewhat different energies; placing them in one energy block without specifying any ordering is a convenience which in no significant way affects our discussion. The e_2 level arising from the $d_{x^2-y^2}$ orbitals is expected[19] to be of comparable energy to the lowest π^* carbonyl level. The allowed transitions between the metal orbitals are $e_1 \rightarrow e_2$ ($^1A_1 \rightarrow {}^1E_1$), $e_3 \rightarrow e_2$ ($^1A_1 \rightarrow {}^1E_1$), $e_3 \rightarrow b_2$ ($^1A_1 \rightarrow {}^1E_1$), $e_2 \rightarrow e_2$ ($^1A_1 \rightarrow {}^1B_2$), and $a_1 \rightarrow b_2$ ($^1A_1 \rightarrow {}^1B_2$); the first three are x, y polarized and the last two are z polarized. Looking more closely at the two z-polarized transitions, $e_2 \rightarrow e_2$ should be at higher energy and should be much weaker than $a_1 \rightarrow b_2$. On the evidence, then, band II is assigned as $a_1 \rightarrow b_2$, which is the allowed transition between the metal–metal σ bond and its corresponding antibonding orbital [$d\sigma$(M–M) $\rightarrow$ $d\sigma^*$(M–M)]. In Mulliken[23] notation, this is an $N \rightarrow V$ transition. It follows that band I is reasonably assigned as the $d\pi \rightarrow d\sigma^*$ transition $e_3 \rightarrow b_2$. We infer therefore that the $d\sigma$ orbital is effectively placed slightly lower in energy than the $d\pi$ levels for the $Mn_2(CO)_{10}$ complex.

S_{zz}, as determined in this near-ultraviolet experiment, is about 0.1 for a path length of 0.025 mm. It is encouraging that the same value was obtained in the infrared work.

The electronic absorption bands in the technetium and rhenium decacarbonyls, which correspond to band II in $Mn_2(CO)_{10}$, are located at 31,700 and 32,300 cm^{-1}, respectively.[24] These bands are similarly assigned as $d\sigma$(M–M) $\rightarrow$ $d\sigma^*$(M–M) transitions.

Concluding Remarks

As is evident from the above examples, the use of nematic solvents provides a quick, simple method for obtaining the polarizations of both electronic and infrared absorption bands. Only a small amount of solute is needed and the polarization data obtained are readily interpretable. It appears that the most important application of the method we have described is in obtaining polarization data for very intense spectral bands. Consider, for example, the determination of the polarization of band II ($\epsilon \sim 2 \times 10^4$) in $Mn_2(CO)_{10}$ by a single-crystal technique. If a pure single crystal were used, it would have to be only about 0.1 μ in thickness in order to obtain reasonable absorbance data. Preparing such a thin crystal and mounting it, while possible,[25] are not simple tasks. Furthermore, the alternative of finding a transparent, nonperturbing single-crystal host is not always possible.

In single-crystal infrared work, there is the additional problem of several site symmetries and of distortions that can give rise to more than the number of bands predicted by simple point group theory. As a result, polarization data in some cases may not be readily analyzed. The nematic liquid crystal method has the advantage of determining the polarizations of bands in a solution environment and allows a more straightforward interpretation.

The technique presented here offers several advantages over the oriented frozen glass method used by Sackmann;[5] this latter method requires that the sample be placed in a large magnetic field (~20 kG) for several hours to induce orientation, after which the spectra must be recorded at −50°. In addition to avoiding these complications, the use of a nematic solution eliminates the scattering problem found by Sackmann[5] in the frozen glasses.

Undeniably, the present technique has some limitations, the principal ones being the solubility and thermal stability of the solute in the nematic solvent we have used. The recent upsurge of interest in liquid crystals, however, promises to provide other nematic systems which should extend the range of applicability. Several mixtures are known to be nematic at room temperature and these could prove useful in eliminating the thermal decomposition problems which we have encountered with several compounds. Extension of the technique to include lyotropic nematic solvents (essentially concentrated soap solutions) should prove of considerable value in extending the uv cutoff beyond the present limitation of 30,000 cm^{-1}.

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