AIP | The Journal of Chemical Physics

Electronic States of HNCO, Cyanate Salts, and Organic Isocyanates. I. Luminescence Studies

J. W. Rabalais, J. R. McDonald, and S. P. McGlynn

Citation: The Journal of Chemical Physics **51**, 5095 (1969); doi: 10.1063/1.1671907
View online: http://dx.doi.org/10.1063/1.1671907
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/51/11?ver=pdfcov
Published by the AIP Publishing

approximation of a "frozen" nonexcited valence electron, are all in agreement with the usual HF-type calculations. Thus the author feels that the results for Ca are essentially what one would obtain with the much more complex HF calculations.

There are many different variations on Cohen and Kelly's basic idea which could be used to investigate the higher excited states "freezing" one of the valence electrons in an excited mp or md state. Thus, to within the expected accuracy of the HF method, the pseudopotential method should be useful in investigating the complete spectra of the two-valence atoms. Of course, very accurate values will be obtained only when correlation effects are introduced into the pseudopotential method.[7]

As with the one-electron problems,[3,4,6] the pseudopotential method reduces the amount of calculations and also allows one to proceed from one excited state to another (within a given l value) by using the total modified potential V_M without having to make initial estimates of the higher excited wavefunctions. For the first level of each l value in the present work the initial starting pseudowavefunction was taken to be the corresponding pseudowavefunction of the one-electron atom; i.e., the Be $2s2p$ $^{1,3}P$ states were started with the Li $2p$ pseudowavefunction, the Ca $4s3d$ $^{1,3}D$ states with the K $3d$ pseudowavefunction. However, in general the rate of convergence and the self-consistency of the final wavefunctions were not quite as good as in the one-electron problems. Also, for the $^{1,3}S$ states of both Be and Ca when going from the first to the second energy levels the use of the total modified potential of the first level as an initial approximation to the second level broke down. For these particular cases initial wavefunctions had to be used.

ACKNOWLEDGMENTS

The author is grateful to the State University of New York, Maritime College, for use of their IBM 1130 and to the Research Foundation of the State University of New York for a two-month summer faculty fellowship during which time most of the calculations were done. The author is also grateful to Dr. Levente Szasz for discussions on the work.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 51, NUMBER 11 1 DECEMBER 1969

Electronic States of HNCO, Cyanate Salts, and Organic Isocyanates. I. Luminescence Studies*

J. W. Rabalais, J. R. McDonald, and S. P. McGlynn

Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803

(Received 25 June 1969)

The phosphorescence spectra and lifetimes of the cyanate salts of Na^+, K^+, Cd^{2+}, Ag^+, Hg^{2+}, and Pb^{2+} have been measured. Similar measurements have been made on CH_3NCO, CH_3CH_2NCO, C_6H_5NCO, and HNCO. The results of these studies indicate that the lowest-energy excited state of the cyanate ion and the covalent isocyanates is of $\cdots (\pi)^3(\pi^*)^1$ MO excitation type: This state is $^3\Sigma^+(C_{\infty v})$ in NCO^-, $^3A'(C_s)$ in HNCO and the alkyl isocyanates, and $^3A_1(C_{2v})$ in phenyl isocyanate. Fluorescence is observed only from the phenyl isocyanate and is assumed to initiate in an excited state which has dominant excitation amplitude on the phenyl moiety. Vibrational structure observed in the phosphorescence of NaOCN and C_6H_5NCO is analyzed, and similarities in the spectra are pointed out. A heavy-atom spin–orbit coupling effect is observed in the cyanate salt series. Spin–orbit coupling calculations have been performed on NCO^-, linear and bent. A phosphorescence lifetime of $\sim$0.12 sec, in good agreement with experiment, is predicted for the $^3\Gamma_{\pi\pi^*} \rightarrow {}^1\Gamma_1$ transition.

INTRODUCTION

The lowest-energy electronic-excited state of simple polyatomic inorganic anions has been found[1–5] to be the T_1 triplet state. The present study, which follows along the same lines,[1–5] is concerned with the phosphorescence of HNCO, cyanate salts, and some organic isocyanates.

Phosphorescence in the near-ultraviolet and visible regions is a fairly general characteristic of polyatomic ionorganic ions.[2] Thus, the cyanate ion exhibits a distinct phosphorescence at $\sim$415 mμ. This emission is relatively intense in the lighter metal salts and has a lifetime τ_p of the order of 10^{-1} sec. The vibrational structure associated with this phosphorescence indicates that it originates in the NCO^- ion. The organic isocyanates also phosphoresce in the same region as NCO^- but with a lifetime which is somewhat longer (i.e., $\tau_p \simeq 1$ sec).

---

* This research was supported by contract between the United States Atomic Energy Commission—Biology Branch and the Louisiana State University.

[1] H. J. Maria, A. Wahlborg, and S. P. McGlynn, J. Chem. Phys. **49**, 4925 (1968).

[2] H. J. Maria, B. N. Srinivasan, and S. P. McGlynn, Proc. Intern. Conf. Molecular Luminescence, Loyola Univ. Chicago, 1968, 787 (1969).

[3] H. J. Maria, A. T. Armstrong, and S. P. McGlynn, J. Chem. Phys. **48**, 4694 (1968).

[4] H. J. Maria, A. T. Armstrong, and S. P. McGlynn, J. Chem. Phys. **50**, 2777 (1969).

[5] J. R. McDonald, V. M. Scherr, and S. P. McGlynn, J. Chem. Phys. **51**, 1723 (1969).

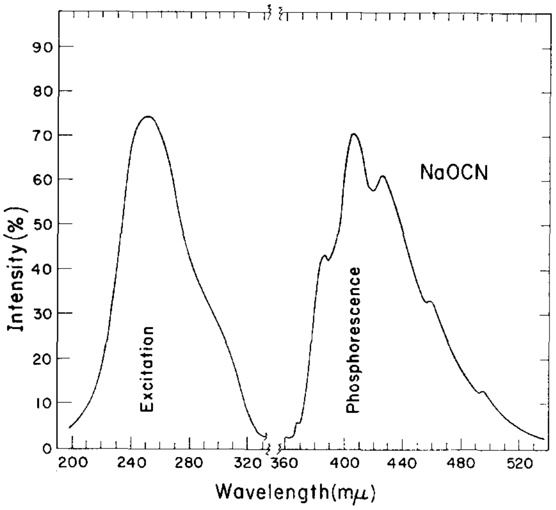

FIG. 1. Phosphorescence emission and excitation spectra of NaOCN at 77°K. The spectra are identical in polycrystalline samples, in frozen-water solutions, or in alcoholic glasses. The slitwidth used in resolving the phosphorescence was 0.26 mm.

EXPERIMENTAL

Instrumental Measurements

All measurement techniques were identical to ones already described.[5]

Compounds and Solvents

Extensive precautions were taken in the preparation and purification of all compounds in order to ensure that the phosphorescence spectra and decay curves would be free from impurity effects.

NaOCN and KOCN

Sodium cyanate (E. H. Sargent Company) and potassium cyanate (J. T. Baker Company) were purified by five recrystallizations from methanol–water mixtures. In the first two crystallizations, the solutions were allowed to begin precipitation and were then screened through millipore filters designed to eliminate particles larger than 0.45 μ. In all crystallizations, only small amounts of compound were claimed and precipitation was allowed to progress slowly.

$Cd(NCO)_2$, $Hg(NCO)_2$, $Pb(NCO)_2$

The cadium, mercuric, and lead cyanates were prepared by mixing solutions containing stoichiometric quantities of the metallic chloride and KOCN. The precipitated metallic cyanate was washed with warm water, followed by acetone, and dried under vacuum. The solubilities of the cadium, mercuric, and lead cyanates could be classified as slightly soluble, almost insoluble, and quite insoluble, respectively.

Ag(NCO)

Silver cyanate (Eastman Company) was purified by dissolving it in a water–ammonia solution and allowing it to evaporate slowly for about three weeks. The large flat crystals which precipitated could be seen to decompose to free silver in very short times, even in the dark and under vacuum. Identical absorption and emission spectra were observed from white freshly prepared samples and from samples which obviously contained free silver.

HNCO

Isocyanic acid was prepared[6] by allowing a freshly prepared saturated solution of KOCN to drop slowly into 90% phosphoric acid *in vacuo*. The gaseous products were condensed in a 77°K cold trap. The impurities—mostly CO_2—were pumped off at trap temperatures near −40°C. The HNCO vapor samples were collected in sealed cells by raising the trap temperature to ∼0°C.

CH_3CH_2NCO, CH_3NCO, and C_6H_5HCO

Ethyl-isocyanate (Aldrich Chemical Company) and methyl- and phenyl-isocyanate (Ott Chemical Company) were treated with 5 mole% of dimethylaniline to remove hydrolyzable chlorides; they were then vacuum distilled. Since these cyanates react readily with water, all handling was done in a dry box.

Solvents

EPA (ether, isopentane, and ethyl alcohol: 5/5/2 by volume), mixed alcohol (methyl, ethyl, and propyl alcohols), and 3-methylpentane were obtained, as the fluorimetric grade, from the Hartman–Leddon Company and used without further purification. The water used had a resistivity greater than 1 MΩ/cm.

All purified compounds were stored in the dark *in vacuo* until immediately prior to use. Freshly prepared solutions were used in all spectroscopic measurements.

TABLE I. Vibrational structure in the phosphorescence of NaOCN.

Assignment	λ(mμ)	$\bar{\nu}$ (cm⁻¹)	$\Delta\bar{\nu}$ (cm⁻¹)	Difference (cm⁻¹)
ν_{00}	367	27 248		
			1344/1	1344
ν_{10}	386	25 904		
			2617/2	1309
ν_{20}	406	24 631		
			3829/3	1276
ν_{30}	427	23 419		
			5462/4	1365
ν_{40}	459	21 786		
			7005/5	1401
ν_{50}	494	20 243		
				Average: 1339 cm⁻¹

---

[6] B. Krakow, R. C. Lord, and G. O. Neely, J. Mol. Spectry. **27**, 148 (1968).

Matrices

Solutions in mixed alcoholic solvent or in EPA congealed to transparent glasses of good optical quality at 77°K. These are "true solutions." "Frozen-water solutions" rarely formed uniform glasses when cooled to 77°K; they contained regions of true solution interspersed with regions of suspended solute microcrystals. The emission of pure polycrystalline samples or of the solute in an EPA or mixed alcohol glass were identical.

EXPERIMENTAL RESULTS

Emission Spectra

The phosphorescence of HNCO gas dissolved in a 3-methylpentane glass at 77°K was observed. The emission centered at ~430 mμ and the excitation centered at ~260 mμ. However, since the emission was quite weak and since obvious polymerization had occurred in the solution prior to glassification, we made no attempt to resolve these spectra further.

NaOCN, KOCN, and $Cd(NCO)_2$ are reasonably soluble in water and mixed alcohols and phosphorescence emission spectra of frozen-water solutions, alcoholic glasses, and crystalline or polycrystalline samples can be detected. Phosphorescence spectra, excitation spectra, and phosphorescence lifetimes observed under these different conditions are identical.

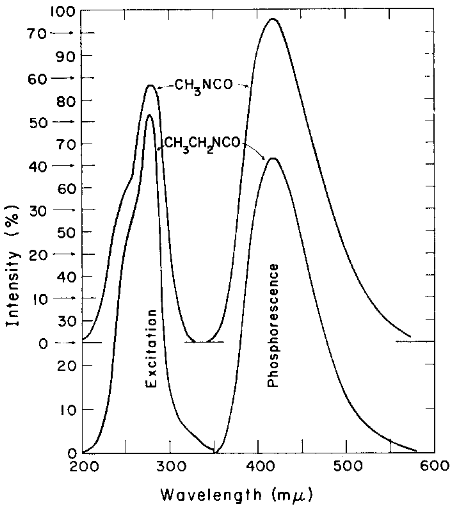

FIG. 3. Phosphorescence emission and excitation spectra of CH_3HCO and CH_3CH_2NCO in EPA glass at 77°K.

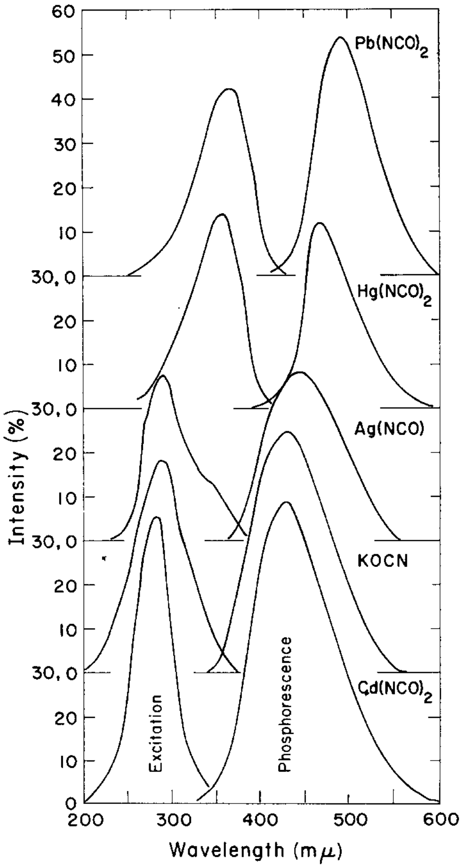

FIG. 2. Phosphorescence emission and excitation spectra of some cyanate and isocyanate salts at 77°K. All spectra are from Polycrystalline samples and are identified in the diagram.

$Hg(NCO)_2$, $Ag(NCO)$, and $Pb(NCO)_2$, however, are quite insoluble in both water and in mixed alcohols; in these instances, it was difficult to increase the solute emission level above the solvent background and we have had to place reliance on the emission of the polycrystalline materials.

The luminescence emission and excitation spectra of NaOCN crystals at 77°K are shown in Fig. 1. The vibrational structure is analyzed in Table I; it is identical in frozen-water solutions, in alcoholic glasses, and in polycrystalline samples. The weak peak at 27 248 cm^{-1} is assumed to be the 0–0 band of a progression with an average spacing of 1339 cm^{-1}. This probably corresponds to the ground-state symmetrical stretching frequency[7] of NaOCN, which is 1305 cm^{-1}.

The phosphorescence and excitation spectra of KOCN, $Cd(NCO)_2$, $Ag(NCO)$, $Hg(NCO)_2$, and $Pb(NCO)_2$ are shown in Fig. 2. None of these spectra shows vibrational structuring. The maxima are collected in Table III. The maxima for NaOCN, KOCN, and $Cd(NCO)_2$ occur at approximately identical wavelengths whereas those of $Ag(NCO)$, $Hg(NCO)_2$, and $Pb(NCO)_2$ are increasingly red-shifted. This red shift is readily rationalized as follows: By observing the water solubility of these salts, we conclude that the covalency of these compounds increases in the order:

$$NaOCN \simeq KOCN < Cd(NCO)_2 < Ag(NCO) < Hg(NCO)_2 < Pb(NCO)_2.$$

Covalent compounds involving the NCO^- group are

---

[7] T. C. Waddington, J. Chem. Soc. **1959**, 2499.

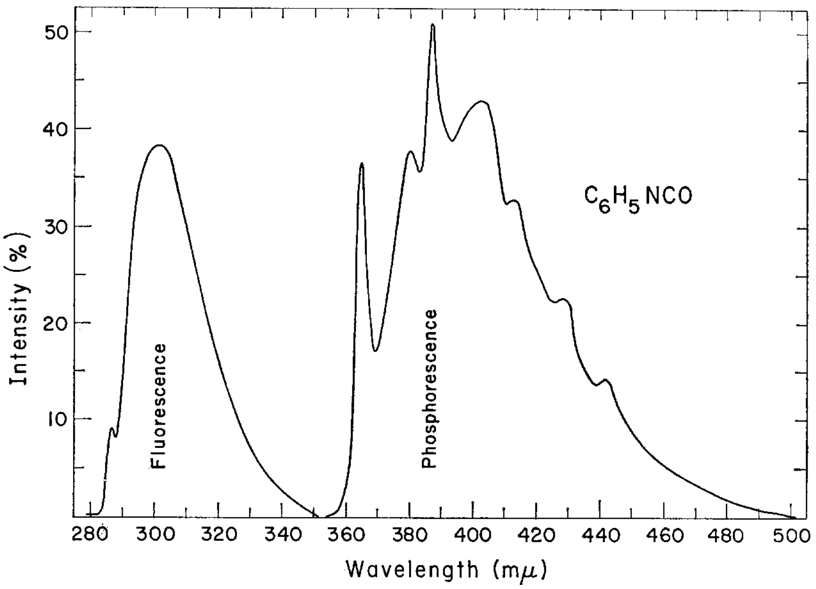

FIG. 4. Total emission spectra of phenyl isocyanate in EPA glass at 77°K. The slitwidth used in resolving these spectra was 0.26 mm.

more stable in the N-bonded (isocyanate) form.[8] Thus the red shift is attributed to an increase in the covalency of these salts or, more specifically, to an increase in the covalent isocyanate character relative to the ionic character.

The phosphorescence and excitation spectra of CH_3NCO and CH_3CH_2NCO are shown in Fig. 3; they are identical and neither compound exhibits any vibrational structure. These spectra were obtained from dilute solutions in EPA glass.

Neither the cyanate salts nor the two alkyl isocynates studied had any detectable fluorescence. If these compounds do fluoresce, their intensities are at least one order of magnitude less than that of the phosphorescences.

The total emission spectrum of phenyl isocyanate is shown in Fig. 4. The vibrational structure of this phosphorescence is analyzed in Table II. The 0, 0 band at 27 435 cm^{-1} is the origin for a progression with 1615 cm^{-1}. Another progression of 1445 cm^{-1} is observed whose origin is displaced 1119 cm^{-1} from the 0, 0 band. The 1615-cm^{-1} mode corresponds to the a_1 symmetric stretching fundamental in the ground state[9] which is productive of the Raman band at 1596 cm^{-1} and the infrared-active band at 1588 cm^{-1}. The 1119-cm^{-1} probably corresponds to the phenyl isocyanate a_1 vibration[9] of 1125 cm^{-1}. The second progression in the 1445-cm^{-1} mode corresponds to the a_1 fundamental (symmetric –NCO stretch) whose wavenumber is 1443 cm^{-1} in the Raman (or 1448 cm^{-1} in the infrared)[9]; this progression is probably vibronically induced.

The maximum in the phosphorescence spectra of CH_3NCO and CH_3CH_2NCO is red-shifted relative to that of phenyl isocyanate. Since the –NCO group is a luminophoric group, it is difficult to understand why emission from C_6H_5NCO should occur at higher energies than that of the alkyl isocyanates. This point will be explained later using quantum-chemical considerations. However, we do wish to note that similar effects are observed in the phosphorescences of benzoic acid and formic acid.[10]

TABLE II. Vibrational structure[a] in the phosphorescence of phenyl isocyanate in EPA at 77°K.

Progression A	Progression B	λ (Å)	ν (cm^{-1})	
ν_{00}^A		3645	27 435	1119
	ν_{00}^B	3800	26 316	1(1622)
ν_{10}^A		3874	25 813	1(1440)
	ν_{10}^B	4020	24 876	2(1611)
ν_{20}^A		4130	24 213	2(1449)
	ν_{20}^B	4270	23 419	3(1612)
ν_{30}^A		4425	22 599	

[a] The vibrational analysis as given here shows progressions of 1615 cm^{-1} and 1445 cm^{-1}, the latter of which is displaced by 1119 cm^{-1} from the origin and is assumed to be vibronically induced. Alternately, the emission can be considered as three vibrational progressions of frequency 1119, 1445, and 1615 cm^{-1}, the broad peak at 400 mμ (Fig. 4) being assumed to resolve into two subpeaks. These two peaks would then be interpreted as 2×1119 and 1119+1445 cm^{-1} overtone and combination bands, respectively.

---

[8] For this reason the sodium and potassium salts are written as normal cyanates whereas the heavier metal salts are written as isocyanates—the intermediate cases existing as partially ionic and partially covalent entities. The covalent salts are of the iso-linkage. Indeed, cyanic acid is unkown, but isocyanic acid is quite common.

[9] C. V. Stephenson, W. C. Coburn, Jr., and W. S. Wilcox, Spectrochim. Acta **17**, 933 (1961).

[10] H. J. Maria and L. W. Johnson (unpublished work).

TABLE III. Phosphorescence lifetimes and maxima of the excitation and phosphorescence spectra of cyanate salts, HNCO, and some organic isocyantes.

Compound	Matrix	Excitation maximum (mμ)	Phosphorescence maximum (mμ)	τ_p (sec)
NaOCN	Polycrystalline	248	406	0.21
	Alcoholic glass	248	406	0.16
	Frozen-water soln.	245	406	0.17
KOCN	Polycrystalline	285	425	0.37(59%) and 4.7×10^{-2}(41%)
	Alcoholic glass	280	424	···
	Frozen-water soln.	283	424	0.35(67%) and 5.5×10^{-2}(33%)
$Cd(NCO)_2$	Polycrystalline	280	425	0.16(70%) and 2.2×10^{-2}(30%)
Ag(NCO)	Polycrystalline	285	440	···
$Hg(NCO)_2$	Polycrystalline	355	460	$\sim3\times10^{-2}$
$Pb(NCO)_2$	Polycrystalline	363	490	$\sim7\times10^{-3}$
CH_3NCO	EPA glass	277	418	2.05
CH_3CH_2NCO	EPA glass	277	420	1.74
C_6H_5NCO	EPA glass	285	387	3.15
HNCO	3-Methylpentane glass	260	430	···

The fluorescence of phenyl isocyanate exhibits no vibrational structure (within our resolution limits) with the exception of a probable 0, 0 band at ~2860 Å which corresponds to the 0, 0 band observed in absorption[11] at ~2830 Å. Since no fluorescence has been observed from the cyanate salts or alkyl isocyanates, we conclude that the phenyl moiety is responsible for the fluorescence of phenyl isocyanate. Indeed, quantum-mechanical calculations show that the wavefunction for the first excited singlet state (the fluorescent state) has a node through the -NCO group and thus has only phenyl character.

Excitation Spectra

The excitation spectra were recorded by monitoring the excitation wavelength while the emission monochromator was fixed on the phosphorescence intensity maximum. The maxima in the excitation spectra coincide with the edge of the $S_0 \rightarrow T_1$ absorption in most of the compounds; however, the absorption spectra do appear to differ from the excitation spectra. These differences are expected and are attributed to the following: The excitation spectra were obtained with an Osram xenon XBO 150-W lamp and are uncorrected for variances in lamp output. The intensity of the xenon lamp decreases rapidly below 250 mμ, thus causing the excitation spectra to inevitably drop off in this region. Correcting these spectra for lamp output is not feasible because this requires the preparation of samples of known absorptivity or concentrations. Most of the samples are insoluble in solvents which form good glasses at 77°K, making it necessary to use crystalline samples in which the absorptivity or concentration is not known.

The fact that the excitation spectra did not match with the absorption spectra induced us to investigate the alkyl- and arylisocyanates. The similarities between the emission and excitation spectra of the inorganic and organic isocyanates gives additional confidence in our assignments.

Phosphorescence Lifetimes

The mean phosphorescence lifetimes of the compounds discussed above are presented in Table III. The lifetimes of NaOCN and KOCN are not dependent on the matrix; in other words, they are more or less the same in the polycrystalline salt, in frozen-water solution, or in mixed alcohol glass. Because of low solubilities and solvent-background decay, lifetimes for the other salts are reliable only in the polycrystalline samples. The lifetimes of the organic isocyanates were obtained in an EPA glass. The lifetime of Ag(NCO) is not reported because its inherent weakness made elimination of background decay impossible.

Five observations result from the decay data of Table III:

(a) The lifetimes of NaOCN, KOCN, $Cd(NCO)_2$, and the organic isocyanates are too long to be typical of either $\pi^* \rightarrow n$ or $n^* \rightarrow \pi$ phosphorescences. They pertain, almost certainly, to $\pi^* \rightarrow \pi$ molecular orbital type luminescences.

(b) A "heavy-atom effect" is exhibited[11] by the luminescence of the salts. The lifetimes decrease as the atomic number of the associated metal cations increase. It is assumed that this is caused by enhanced spin-orbit coupling.

---

[11] (a) S. P. McGlynn, T. Azumi, and M. Kasha, J. Chem. Phys. **40**, 507 (1964). (b) V. Ramakrishnan, R. Sunseri, and S. P. McGlynn, J. Chem. Phys. **45**, 1365 (1966). (c) S. P. McGlynn, J. Daigre, and F. J. Smith, J. Chem. Phys. **39**, 675 (1963).

(c) With the exception of KOCN and $Cd(NCO)_2$, all lifetime curves are either exponential or closely so. KOCN and $Cd(NCO)_2$ luminescences exhibit two lifetime components. The existence of these two components is not readily interpreted, but may be attributed to ionic and covalent emitting entities.

(d) The lifetime of CH_3NCO is slightly longer than that of CH_3CH_2NCO, in agreement with expectations[12] for highly alkylated molecules.

(e) The lifetime of phenyl isocyanate is longer than any of the other isocyanates. This is attributed to the following: First, there is no alkyl group present as in the other isocyanates; alkyl groups tend to shorten lifetimes[12] because they induce larger Franck–Condon factors. Second, the vibrational structure of the phosphorescence indicates that the phenyl ring as well as the –NCO group is involved in the emission act. In other words, the terminal- and initial-state wavefunctions in the emissive act span the whole molecule and the weak spin–orbit coupling experienced in the phenyl moiety is reflected in the longer lifetime of the phenyl isocyanate.

QUANTUM-CHEMICAL CONSIDERATIONS

A Mulliken–Wolfsberg–Helmholz (MWH) calculation similar to that of McDonald *et al.*[5] was performed on the NCO^- ion. The Clementi double-zeta[13] representation for AO's was employed using the $2s$, $2p_x$, $2p_y$, and $2p_z$ AO's on the N, C, and O atoms as the basis atomic orbital set. The computation was processed to charge self-consistency and a set of molecular orbitals was obtained; these were disposed energetically in a manner identical to that for the NCS^- ion (see Fig. 5 of Ref. 5). The important result which emerges is that the lowest-energy transition is predicted to occur from a doubly degenerate set of π MO's to a doubly degenerate set of π^* MO's and to be located at ~ 285 mμ. The equilibrium ground state of NCO^- and –NCO of covalent isocyanate moecules is predicted to be linear, whereas the equilibrium excited state is predicted[14,15] to be bent with an NCO angle of $\sim 129°$. Since absorption involves the linear NCO^- configuration and since emission should involve the bent NCO^- configuration, a considerable Stokes shift between the $T_1 \rightarrow S_0$ emissive event and the $T_1 \leftarrow S_0$ absorptive event is expected and is observed. Franck–Condon forbiddenness of origins is expected (with very little 0, 0 intensity observable), which is, indeed, the case in Figs. 1–3.

VESCF and configuration-interaction calculations have been performed on these molecules.[16] All electronic states resulting from $\pi \rightarrow \pi^*$ MO excitations were calculated and the lowest $\sigma \rightarrow \pi^*$ states estimated from MO computations.

The results of these calculations on NCO^- show that the first excited singlet state is $^1\Sigma^-$ and the first triplet state is $^3\Sigma^+$. Similar computations on HNCO (linear –NCO) and HNCO (–NCO angle = 129°) indicate that the first excited singlet state is $^1A''$ (correlating with the $^1\Sigma^-$) and the first triplet state is $^3A'$ (correlating with the $^3\Sigma^+$). These $^1A''$ and $^3A'$ states are predicted to be at ~ 5.95 and ~ 2.11 eV, respectively, in the case of the linear –NCO and ~ 3.26 and ~ 0.42 eV, respectively, in the bent –NCO. These results are applicable to NCO^- and the alkyl isocyanates also. Although the energies of the triplet states are too low and the change in energy upon bending is certainly exaggerated, the results do indicate that the first excited singlet and triplet states are indeed lowered energetically upon bending the –NCO group.

Computations on C_6H_5NCO indicate that the first excited singlet state is $^1B_1$ whereas the first triplet state is $^3A_1$; these are predicted to be at ~ 4.58 and ~ 1.92 eV, respectively. The large amount of conjugation between the phenyl ring and the –NCO group indicates that the first excited states are not bent; that is, the molecule retains its C_{2v} symmetry in the lower-energy excited states.

We now direct attention to the fact that the phosphorescence maxima of CH_3NCO and CH_3CH_2NCO are at lower energy than that of phenyl isocyanate. The phosphorescence spectrum of C_6H_5NCO shows a strong 0, 0 band, indicating that the geometry of this molecule (C_{2v}) is similar in the ground and triplet state. This is also borne out by quantum-chemical calculations.[16] The phosphorescence spectra of CH_3NCO and CH_3CH_2NCO have a forbidden origin indicating that the excited state is strongly bent while the ground state is

TABLE IV. Spin–orbit coupling in linear NCO^-. [The $^1\Sigma^+ \leftarrow {^3\Sigma^+}$ transition is composed of the two configurations indicated. The z axis lies along the N–C–O axis. The (x, y) axes are perpendicular to z.]

Configuration		SOC operator	Conferred transition moment		
			M_x	M_y	M_z
$\pi_x \rightarrow \pi_x^*$	$^1\Sigma^+ \leftarrow {^3\Sigma^+}$	$\mathcal{H}_x$	0.0	0.0	0.0
		$\mathcal{H}_y$	2.28×10^{-4}	0.0	0.0
		$\mathcal{H}_z$	0.0	0.0	0.0
$\pi_y \rightarrow \pi_y^*$		$\mathcal{H}_x$	0.0	-2.28×10^{-4}	0.0
		$\mathcal{H}_y$	0.0	0.0	0.0
		$\mathcal{H}_z$	0.0	0.0	0.0
			2.28×10^{-4}	-2.28×10^{-4}	0.0

$\mathbf{M}^2 = \frac{1}{2}(\mathbf{M}^2_{\pi x \rightarrow \pi x^*} + \mathbf{M}^2_{\pi y \rightarrow \pi y^*})$
$f = 1.5 \times 10^{-8}$
$\tau = 0.13$ sec

---

[12] J. W. Rabalais, H. J. Maria, and S. P. McGlynn, J. Chem. Phys. **51**, 2259 (1969).

[13] E. Clementi, IBM Research Paper R-J-256, 6 September 1963.

[14] R. N. Dixon and G. H. Kirby, Trans. Faraday Soc. **64**, 2002 (1968).

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

[16] J. W. Rabalais, J. R. McDonald, and S. P. McGlynn, J. Chem. Phys. **51**, 5103 (1969), following article.

TABLE V. Spin–orbit coupling in two states of bent NCO^- (129°). [The molecule is in the (x, y) plane with the z axis perpendicular to this molecular plane.]

State	Configuration	SOC operator	Conferred transition moment M_x	M_y	M_z
$^3A'$	$\pi\rightarrow\pi^*$	$\mathcal{H}_x$	0.0	0.0	3.416×10^{-4}
		$\mathcal{H}_y$	0.0	0.0	-5.845×10^{-4}
		$\mathcal{H}_z$	0.0	0.0	0.0
		M	0.0	0.0	-2.429×10^{-4}
		f			1.78×10^{-8}
		τ (sec)			0.11
$^3A''$	$\sigma\rightarrow\pi^*$	$\mathcal{H}_x$	0.0	0.0	-2.231×10^{-5}
		$\mathcal{H}_y$	0.0	0.0	3.400×10^{-4}
		$\mathcal{H}_z$	-2.020×10^{-4}	1.217×10^{-3}	0.0
		M	-2.020×10^{-4}	1.217×10^{-3}	3.177×10^{-4}
		f	1.238×10^{-8}	4.46×10^{-7}	3.04×10^{-8}
		τ (sec)	0.16	0.0044	0.064

linear. Indeed, quantum-chemical calculations[16] show that the first triplet state of alkyl isocyanates can obtain a much lower energy by bending. Therefore, the maximum in the alkyl isocyanates is red-shifted with respect to that of phenyl isocynate because of the greater Franck–Condon forbiddenness of the origin in the former case. The origins (i.e., presumed 0, 0 bands) of the phosphorescence of both types of molecule are very nearly of equal energy.

We will now consider the triplet-state emissive lifetimes. McDonald *et al.*[5] have shown that the first triplet state of $NCS^-(^3\Sigma^+)$ can obtain an (x, y) allowedness by spin–orbit coupling with a nominal $^1\Pi$ state and that the intrinsic emissive lifetime should be of the order of 1 sec. Numerical calculations of the phosphorescence lifetime of the $^3\Sigma^+$ state of NCO^- have been performed as follows: Transition moments, both $S_0\rightarrow S_j$ and $T_1\rightarrow T_j$, were calculated after transformation of all MO's to a Löwdin basis; the procedure followed has been described by Cusachs and Trus.[17] One-center spin–orbit coupling calculations were then performed as described by Carroll *et al.*[18] Thus, the AO basis set consisted of 12 orbitals or, in terms of Slater functions, 24 Slater functions. This resulted in 12 MO's, 6π and 6σ. All possible excited configurations resulting from these MO's, namely 33, were considered and the spin–orbit and transition-moment computations were performed for all possible spin-allowed transitions and all possible spin–orbit mixings.

Since the $^3\Sigma^+$ state of NCO^- is bent, calculations were performed on both linear NCO^- and bent NCO^- (129°); the results of these computations are presented in Tables IV and V. The results for the $^3\Sigma^+$ and $^3A'$ states, which arise from $\pi\rightarrow\pi^*$ MO excitations, indicate that the phosphorescence lifetime of linear NCO^- and bent NCO^- are approximately the same, ~0.12 sec, with the phosphorescence from linear NCO^- being polarized perpendicular to the molecular axis while that of bent NCO^- is polarized perpendicular to the molecular plane. Thus, the phosphorescence lifetime is not much effected by lowering the symmetry of the first triplet state from $^3\Sigma^+$ $(C_{\infty v})$ to $^3A'$ (C_s).

Similar calculations were performed on the $^3A''$ state of bent NCO^- which arises from a $\sigma\rightarrow\pi^*$ MO excitation. The results, shown in Table V, incidate that the phosphorescence has components of all three polarizations with the lowest component being several milliseconds. Thus, this calculation is additional evidence that the first triplet state of NCO^- must be $^3\Sigma^+(C_{\infty v})$ or $^3A'(C_s)$ arising from a $\pi\rightarrow\pi^*$ MO excitation.

DISCUSSION

The results of our experimental work reveal that the –NCO moiety is luminophoric. This is concluded from the following observations:

(a) The phosphorescence from cyanate salts is exhibited by polycrystalline samples and true solution phases. Thus, the luminescence is not of a solid-state defect nature.

(b) That the emission arises from a chemical contaminant is highly unlikely since it has been observed in cyanate salts, organic isocyanates, and HNCO. These compounds have originated from different source materials and have undergone extensive and different purification procedures.

(c) The emission from alkyl isocyanates is at

---

[17] L. C. Cusachs and B. L. Trus, J. Chem. Phys. **46**, 1532 (1967).

[18] D. G. Carroll, L. G. Vanquickenborne, and S. P. McGlynn, J. Chem Phys. **45**, 2777 (1966).

approximately the same wavelength as the cyanate salts indicating that the –NCO entity is responsible for this emission.

(d) Emission has been observed from HNCO at approximately the same wavelength as the alkyl isocyanates and cyanate salts.

(e) The single vibrational progression observed in the emission of NaOCN agrees with the symmetrical ground-state stretching frequency of NCO^-.

(f) The emission from phenyl isocyanate is shifted from that of benzene to approximately the same wavelength as the alkyl isocyanates and the cyanates salts indicating that the –NCO entity is participating, along with the phenyl ring, in the emission process. The vibrational analysis shows two progressions which are readily matched with ground-state frequencies of C_6H_5NCO. One of these corresponds to a symmetric ring stretching frequency and the other to a symmetric –NCO stretching frequency. The latter progression has the same band shape and contour as the progression observed in the NaOCN emission.

The emitting state in these compounds must be a triplet state for the following reasons:

(a) The lifetimes observed are much too long to be fluorescence lifetimes; therefore, they must be intrinsic molecular phosphorescence from a triplet state.

(b) The lifetimes decrease as the atomic number of the associated metal cation increases. This is a "heavy-atom spin–orbit coupling effect" which is common in molecular phosphorescence.

(c) VESCF and configuration-interaction calculations[11] show that the lowest excited electronic state of all the molecules is a triplet state.

The assignment of the lowest triplet state of all these molecules has been made by means of the configuration-interaction calculations.[16] The phosphorescence is assigned as a $^3\Sigma^+\rightarrow{}^1\Sigma^+$ transition in NCO^-, a $^3A'\rightarrow{}^1A'$ transition in bent NCO, HNCO, and the alkyl isocyanates, and a $^3A_1\rightarrow{}^1A_1$ transition in phenyl isocyante. Since the first triplet state of NCO^- is predicted to be bent, the phosphorescence can be labeled as $^3A'(C_s)\rightarrow{}^1\Sigma^+(C_{\infty v})$. Spin–orbit coupling calculations on the $^3\Sigma^+$ state of linear NCO^- and the $^3A'$ state of bent NCO^- predict a lifetime of ~0.12 sec, in good agreement with experiment. Similar computations on the $^3A''$ state of bent NCO^- predict a lifetime of several milliseconds, thus verifying that the phosphorescence must be $\pi\rightarrow\pi^*$ type and not $\sigma\rightarrow\pi^*$ MO type.

Fluorescence has been observed only from the phenyl isocyanate. We attribute this fluorescence to the phenyl moiety since the wavefunction of the first singlet state $^1B_1$ has a node through the –NCO entity and, thus, contains only phenyl character. The wavefunction of the $^3A_1$ state, however, has ~22% –NCO character in it.

The phosphorescence maxima of the cyanate salts undergoes a red shift as the atomic number of the associated metal cation increases. This red shift parallels the increase in covalency of these salts. Thus, the red shift is attributed to a heavier metal cation and a more covalent salt. These covalent salts are most assuredly of the isocyanate type linkage as discussed earlier.

It has been shown that the first triplet state of phenyl isocyanate, alkyl isocyanates, and cyanate salts are at approximately the same energy with the maxima appearing at different wavelengths due to Franck–Condon forbiddance of the origins.