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Matrix-Isolation Study of the Infrared and Ultraviolet Spectra of the Free Radical NCO

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The free radical NCO is stabilized in sufficient concentration for direct infrared and ultraviolet spectroscopic identification upon vacuum-ultraviolet photolysis of HNCO suspended in various matrix materials at 4° and at 14°K. Observations on the $B(^2\Pi) - X(^2\Pi)$ electronic transition of NCO have been extended to shorter wavelengths than those previously reported. Isotopically substituted NCO has been prepared in supplementary experiments involving the vacuum-ultraviolet photolysis of CO:HN₃ and Ar:HCN:N₂O samples, as well as by the mercury arc photolysis of matrix-isolated samples of NO+N₃CN. The three vibrational fundamentals of ground-state NCO appear at 487, 1275, and 1933 cm⁻¹ in an Ar matrix. The values obtained for the stretching force constants suggest that the carbon-oxygen bond may be somewhat stronger than the carbon-nitrogen bond. There is an appreciable positive stretching-interaction force constant. NCO is found to photolyze when subjected to radiation of wavelength near 2537 Å, leading to the production of N+CO. Reactions occurring in the various systems investigated are discussed.

INTRODUCTION

The ultraviolet spectrum of the free radical NCO has been extensively studied by Dixon.^{1,2} Vibrational and rotational analysis of the $A(^{2}\Sigma^{+})-X(^{2}\Pi)$ transition of NCO,¹ for which absorptions are observed between 4500 and 3600 A, has yielded all three vibrational frequencies for the upper state, as well as detailed information on the behavior of the rotational constants in the various excited vibrational levels of the upper state. Four excited levels of the ground-state bending vibration were also observed, and rotational constants were derived for some of these levels, permitting an estimate of the upper limit of the molecular length but not of the individual bond distances. The pattern of energy levels in the ground electronic state is found to be complicated both by an appreciable vibrationalelectronic interaction, leading to Renner-effect splittings of excited bending vibration levels, and by an exceptionally large spin splitting. Considerably less detailed information could be obtained² on the $B(^{2}\Pi)$ - $X(^{2}\Pi)$ transition of NCO, which was observed in absorption between 2650 and 3200 Å. This transition apparently involves an extended progression in the upper-state stretching frequency, ν_1' , as well as less extensive excitation of the other stretching fundamental, ν_3' . Some of the bands above 33 700 cm⁻¹ appear to be diffuse, suggesting that predissociation of NCO may occur.

Despite the considerable contribution of these two studies, much remains to be learned about the NCO free radical. Among the data of interest are the two heretofore inaccessible ground-state stretching frequencies, confirmation of the postulated predissociation of the $B(^{2}\Pi)$ state, and determination of the predissociation products. Observation of isotopically substituted NCO would aid greatly in estimating the relative strengths of the chemical bonds, since there is evidence that for NCO, as well as for similar species, the stretching-interaction force constant is appreciable.

Studies of NCO isolated in an inert matrix could afford information on these unknowns. Although HNCO, used as an NCO precursor by Dixon,^{1,2} might be expected to provide a suitable photolytic source of NCO for matrix observations, Jacox and Milligan³ have found that the principal product of the photolysis of matrix-isolated HNCO using a medium-pressure mercury arc is HOCN. Apparently, the dominant process at these wavelengths involves the detachment of NH, which recombines with CO to stabilize both HNCO and HOCN.

The subsequent development of light sources suitable for vacuum-ultraviolet photolysis of matrix-isolated samples⁴ has reopened the possibility of using HNCO as a photolytic precursor for NCO. Alternate routes for the production of NCO are provided by the reaction of C atoms, produced on photolysis of cyanogen azide, ⁵⁻⁷ with NO and by the reaction of O atoms with CN in a matrix environment. As is shown, NCO is indeed produced in such experiments, which have yielded considerable new information on this species.

EXPERIMENTAL DETAILS

The synthesis of HNCO for these experiments has been described in an earlier article, as have been the syntheses of normal and isotopically substituted cyanogen azide⁵ and hydrogen cyanide⁸ and of carbon sub-

¹ R. N. Dixon, Phil. Trans. Roy. Soc. (London) Ser. A 252, 165 (1960).

² R. N. Dixon, Can. J. Phys. 38, 10 (1960).

⁸ M. E. Jacox and D. E. Milligan, J. Chem. Phys. 40, 2457 (1964).

⁴D. E. Milligan and M. E. Jacox, J. Chem. Phys. **43**, 4487 (1965). ⁵D. E. Milligan, M. E. Jacox, and A. M. Bass, J. Chem. Phys.

^{43, 3149 (1965).} ⁶ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 44, 2850

^{(1966).}

⁷ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 45, 1387 (1966)

^{(1966).} ⁸ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 278 (1967).

oxide.⁹ HN₃ was conveniently prepared by passing a gaseous mixture of HCl with the matrix material through a column packed with 10-15 cm of finely powdered NaN₃. A sample of $H(^{15}N^{14}N_2)$ (96.8%) was prepared by the reaction of the sodium salt with H_3PO_4 , followed by drying of the resulting sample by passage through a column packed with P2O5. NO and N2O (Matheson Co., Inc.)¹⁰ were used without further purification, except for condensation at 77°K to remove traces of noncondensable material. Ar and N2 used as matrix gases were dried by passage through a P_2O_5 column, and CO was freed of characteristic carbonyl impurities by bubbling through concentrated H₂SO₄. Procedures used in the preparation of ^{13}CO (51.6%) have previously been described.9 Ne was used without further purification. Ar (or Ne, CO, N₂):HNCO samples of mole ratio between 200 and 800 were prepared using standard manometric procedures and were passed through a trap cooled to -70° C to remove further trace impurities before deposition on the cold sample window. CO:HN₃ samples of mole ratio 100 or 200 were deposited directly on the sample window, without use of a cold trap. It was necessary to conduct simultaneous deposition of Ar (or N_2): NO = 100 and Ar (or N_2): $N_3CN = 100$ samples onto the cold window, with mixture occurring at the entrance to the cryostat, only a few centimeters from the cold sample window. Under these conditions, no evidence for the reaction of NO with N₃CN could be detected in the infrared spectrum of the resulting solid sample. Ar:HCN:N₂O samples of mole ratio 200:1:1 were deposited through a -70° C trap.

The cryostats used for these observations are similar to that described by Milligan.¹¹ Samples were deposited on a CsI window for the infrared observations. A cryostat with improved sample block design¹² and a sapphire cold window were used for the ultraviolet observations. Except for Ne matrix observations at 4°K, all studies were conducted at 14°K, the triple point of hydrogen.

Ar(Ne, N₂, CO):HNCO, CO:HN₃, and Ar:HCN: N₂O samples were subjected to direct irradiation through a lithium fluoride or a magnesium fluoride window by a microwave (2450-MHz, 125-W) discharge through hydrogen or through a 10% mixture of hydrogen in helium, found to provide relatively enhanced 1216-Å emission. Typically, simultaneous deposition and photolysis of the sample were conducted to maximize the yield of photolysis products. Samples were

subsequently irradiated with the full light of a mediumpressure mercury arc to investigate the photolytic behavior of the primary products. Samples containing cyanogen azide were first subjected to the intense 2288-Å cadmium arc line to produce NCN,^{6,7} which undergoes photolysis to produce carbon atoms when the sample is subsequently subjected to the 2537-Å radiation of the medium-pressure mercury arc. In some experiments, only mercury photolysis was employed, leading to the same final products but omitting the intermediate stabilization of a high concentration of NCN. For the cadmium and mercury arc photolysis, the cryostat base was rotated to permit irradiation through a lithium fluoride window.

Infrared spectra were recorded on a double-beam, prism-grating spectrometer (Beckman IR-9).¹⁰ Between 400 and 2000 cm⁻¹ the resolution and frequency accuracy under typical scanning conditions are approximately 1 cm⁻¹, and between 2000 and 4000 cm⁻¹, approximately 2 cm⁻¹.

The 1900-5200-Å spectral region was studied using an 0.8-m Ebert-Fastie scanning monochromator¹³ equipped with a 1200-grooves/mm grating blazed at 3000 Å, with 25-µ slits, and with an EMI 6255B photomultiplier.¹⁰ A deuterium background source was used for the 1900-3600-Å spectral region and a tungsten background source for the 3600-5200-Å region. Under typical scanning conditions for the present experiments, the wavelength accuracy is estimated as 2 Å throughout the spectral range observed.

ULTRAVIOLET SPECTROSCOPIC **OBSERVATIONS**

The spectrum obtained for a typical Ar:HNCO sample subjected to vacuum-ultraviolet photolysis is shown in Fig. 1. (In this and subsequent figures, the ordinate scale is linear in percent absorption. For clarity, the zero level of certain traces has been displaced.) Extensive absorptions appear between 4500 and 4000 Å and between 3200 and 2400 Å. As shown by the dotted trace, subsequent photolysis with a medium-pressure mercury arc leads to the disappearance of virtually all of these features; only the moderately intense feature near 3380 Å, contributed by NH,¹⁴ and the less intense feature near 3120 Å, contributed by OH,¹⁵ remain with undiminished intensity. Not shown in Fig. 1 is a broad feature of about 20%peak absorption at 3850 Å. This feature, which maintains a constant intensity on subsequent mercury arc photolysis, is readily recognized as the 0-0 band of the CN $B(^{2}\Sigma^{+}) - X(^{2}\Sigma^{+})$ transition.⁸

The correspondence of the features appearing in the Ar: HNCO experiments with the features reported by

- ¹³ W. G. Fastie, J. Opt. Soc. Am. 42, 641, 647 (1952); 43, 1174 (1953)
- ¹⁴ R. N. Dixon, Can. J. Phys. 37, 1171 (1959).

¹⁵ G. Herzberg, *Molecular Spectra and Molecular Structure*. I. Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc., Princeton, N.J., 1950), p. 560.

⁹ M. E. Jacox, D. E. Milligan, N. G. Moll, and W. E. Thompson, J. Chem. Phys. 43, 3734 (1965). ¹⁰ Certain commercial instruments and materials are identified

in this paper in order adequately to specify the experimental procedure. In no case does such identification imply recommenda-tion or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

¹¹ D. E. Milligan, J. Chem. Phys. 35, 1491 (1961). ¹² D. E. Milligan, M. E. Jacox, and L. Abouaf-Marguin, J. Chem. Phys. 46, 4562 (1967).



Dixon^{1,2} for the two ultraviolet band systems of NCO is shown in Tables I and II, which also include data obtained in experiments on the vacuum-ultraviolet photolysis of HNCO isolated in several other matrix materials. All of the gas-phase transitions listed in Tables I and II arise from the 0, 0^1 , 0 level of the ground state. Gas-phase frequencies chosen for Table I are, except for the 0, 1^1 , 0 level (for which *P*-branch frequencies are given), the values reported by Dixon¹ for the *Q* branch of the most intense component of the

TABLE I. Frequencies (cm⁻¹) of absorption bands assigned to NCO $A(^{2}\Sigma^{+})-X(^{2}\Pi)$ transition.

	Upper level	Gas	Ne matrix	Ar matrix	N2 matrix	CO matrix	
·····				21 957			
	0, 0º, 0	22 800 vs	22 762	22 736	22 956	22 919	
		23 383 m–s					
	0, 1 ¹ , 0	23 459 w-m	23 435 vw				
		23 480 m–s					
	1, 0º, 0	24 089 s	24 032	24 020			
	0, 20, 0	24 185 s	24 136	24 101	24 271	24 271	
	1, 11, 0	24 752 w					
	0, 31, 0	24 879 w					
	0, 00, 1	25 137 s	25 087	25 049	25 277	25 258	
	2, 00, 0	25 364 w					
	1, 20, 0	25 456 w-m					
	0, 40, 0	25 586 w					
	0, 11, 1	25 805 w					
	1, 0º, 1	26 404 m-s					
	0, 20, 1	26 496 m-s					
	0, 0°, 2	27 451 s					

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	G	as*	Ne ma	atrix	Ar mat	rix	$N_2 m$	N_2 matrix		atrix
Upper level	ν	Δ	ν	Δ	ν	Δ	ν	Δ	ν	Δ
	31 565 vw				·			·······		
	31 672 vw									
$0, 0, 0 (R_2)$	31 738 s		31 616 m-s		31 437		31 339		30 970	
$0, 0, 0 (R_1)$	31 753 s		31 646 w, sh							
	31 814 vw									
	31 818 vw									
	32 674 w		32 532 w							
			32 596 sh							
$1, 0, 0 (R_2)$	32 763 s	1025	32 649 m–s	1033	32 374 sh	937	32 364	1025	32 001	1031
$1, 0, 0 (R_1)$	32 822 s	1069	32 716 m	1070	32 490	1053				
	32 903 vw		32 767 vw							
			32 831 vw							
	33 620 w		33 539 vw		33 224 sh					
2, 0, 0 (R_2)	33 725 s	962	33 626 m	977	33 413	1039	33 413	1049	33 103	1102
	33 780 m		33 694 m-s							
2, 0, 0 (R_1)	33 843 s	1021	33 728 m-s	1012	33 525	1035				
	33 897 m									
$0, 0, 1 (R_2)$	34 043 m	2305ь	33 911 m	2295ь	33 740 sh	2303 ^b				
$0, 0, 1 (R_1)$	34 054 m	2301ь								
			34 628 w		34 260 sh					
	34 796 w		34 694 m							
3, 0, 0 (<i>R</i>)	34 870 m	1145, 1027	34 757 m-s	1131, 1029	34 520	1107	34 473	1060	34 260	1157
	34 888 vw				34 592 sh					
	34 906 v w									
1, 0, 1 (R ₂)	35 081 w	1038	34 949 m-s	1038	34 736 sh	996	34 640			

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	G	as*	Ne n	natrix	Ar ma	trix	N ₂ 1	natrix	COr	natrix
Upper level	ν	Δ	ν	Δ	v	Δ	ν	Δ	v	Δ
$\overline{1, 0, 1 (R_1)}$	35 095 w	1041								
	35 158 vw		35 053 w							
	35 160 vw									
			35 263 vw							
			35 539 vw		35 300 sh					
			35 719 sh							
	35 873 w		35 760 m							
4, 0, 0 (<i>R</i>)	35 918 mw	1048	35 800 m	1043	35 589	1069	35 640	1167	35 288	1028
	35 955 w									
			35 912 vw							
2, 0, 1°			35 961 m-s	1012	35 780	1044				
			36 001 sh							
			36 140 vw							
	36 852 vw		36 780 w							
	36 996 vw		36 864 vw							
			36 932 w- m							
5, 0, 0 °	37 158 w	1240	37 010 m-s	1210	36 794	1205	36 700	1060	36 379	1091
3, 0, 1°	37 341 m		37 182 m	1221	36 958 sh	1178				
			37 219 w-m, sh							
			37 804 w							
			37 988 m							
6.0.0			38 048 m	1038	37 782	988	37 753	1053	37 512	1133
., . , .			38 120 vw							
4 Ω 1¢			38 197 m-s	1015	37 997	1039				
2, 0, 1			38 238 m. sh							
7 0 00			, -		39 020	1238	38 929	1176	38 628	1116
80.0					40 068	1048	00727	11.0	30 671	1043
0, 0, 0 -					40 229	1010			07 011	1015
0.0.00					41 022	Q54			4 0 671	1000
7, 0, 0°					42 002	1070			T/ 0/1	1000
10, 0, 0					12 192	1001				
11, U, U ^c					43 103	1091				

TABLE II (Continued)

^a Reference 2. ^b (0, 0, 1)-(0, 0, 0). ^o Proposed assignment.

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NCO $A(2\Sigma^+)-X(2\Pi)$ transition. In Table II, the frequencies given by Dixon² for the R_1 and R_2 bandheads of the NCO $B(2\Pi_i)-X(2\Pi_i)$ transition are given. Except for the broad 21 957-cm⁻¹ band observed in the Ar matrix experiments, all of the features observed between 4000 and 4400 A correspond well with the most prominent NCO bands in this region, with allowance for small matrix shifts.

A similar correspondence is noted between the frequencies of gas-phase NCO bands and the frequencies reported in Table II for the matrix studies. However, in the matrix observations numerous features appear at shorter wavelengths. Somewhat larger matrix shifts are noted for this band system of NCO than for the lower-frequency system. Most of the features appearing in the Ne matrix experiments are very sharp, with half-widths of approximately 40 cm^{-1} . The frequency accuracy is, of course, considerably greater for these observations than for those on the relatively broad features of the other experiments. As shown in Fig. 1, the Ar matrix absorptions are considerably broader. Because of the numerous partially resolved satellite features in this system, it is difficult to estimate a half-width. The half-widths of the absorptions appearing in N2 and CO matrix experiments are even greaterapproximately 250 and 500 cm⁻¹, respectively. There is no significant additional broadening of features appearing at the shorter wavelengths. The relatively small matrix shift observed for both NCO transitions in the Ne matrix experiments, the sharpness of the absorptions, and the detailed correspondence of the frequencies of the observed features with those reported for the gas phase are consistent with the suggestion of Weltner, Walsh, and Angell¹⁶ that the environment provided by a Ne matrix more closely approximates the gas-phase environment than does that provided by heavier matrix materials.

The assignment proposed in Table II for the higherfrequency features must be regarded as tentative. In several instances, band separations (Δ) of approximately 1200 cm⁻¹ are noted in Table II between features assigned to x, 0, 0 and (x-1), 0, 0 upper vibrational levels. Especially for the Ne matrix features, such a discrepancy is greater than the experimental error and suggests either that the bands in question are perturbed or that an alternate assignment should be sought. A possible assignment of some of these features may be to bands of x, 0, y upper levels, y=1 or 2. However, the relative intensities of the bands observed in the N_2 and CO matrix experiments are most consistent with their assignment to a single progression; except for the appearance of a band assigned to the 0, 0, 1 upper vibrational state in the N₂ matrix observations, the features observed in these matrices are unstructured and relatively regularly spaced, with smoothly varying intensities.

¹⁶ W. Weltner, Jr., P. N. Walsh, and C. L. Angell, J. Chem. Phys. 40, 1299_(1964). In all of the matrices studied, the features assigned to NCO are found to disappear completely when the sample is subjected to mercury arc irradiation for a period of 30 to 60 min.

Several other systems in which photoproduction of NCO was believed to be possible were also subjected to ultraviolet spectroscopic observation. In experiments in which HN₃ suspended in a CO matrix was photolyzed with vacuum-ultraviolet radiation, a higher concentration of NCO was noted than in the HNCO photolysis studies. Smaller but significant concentrations of NCO were observed in studies of the vacuum-ultraviolet photolysis of Ar: NO: C₃O₂ and Ar: HCN: N₂O samples and in studies of Ar: NO+Ar: N₈CN samples subjected to irradiation with a medium-pressure mercury arc. In the N₃CN experiments, complete photolytic destruction of NCN is achieved more readily than is that of NCO. Presumably, the intense absorption of CNN at wavelengths shorter than 2450 Å 17 serves to some extent to filter radiation effective in the photolysis of NCO. No features attributable to other products of the reaction of C atoms with NO, such as CNO, were detected in these experiments.

INFRARED SPECTROSCOPIC OBSERVATIONS

Vacuum-Ultraviolet Photolysis of HNCO

The frequencies of features which appear after vacuum-ultraviolet photolysis of Ar:HNCO samples are summarized in Table III. Several of these features have previously been identified³ as fundamentals of the species HOCN. Although they also appear in the present experiments, they are relatively less promi-

TABLE III. Frequencies (cm⁻¹) of infrared absorptions appearing after vacuum-ultraviolet photolysis of matrix-isolated HNCO.

Ar matrix	Ar matrix (50% D)	N2 matrix	Assignment
		461	HOCN
484 sh	484 sh	484	
487	487	490	
541 br	540 w br	170	
011 01	950		DOCN
	1079	1098	HOCN DOCN
1224 sh	1223 sh	1070	HOCN
1224 51	1228 31	1242	HOCN
1275	1220	1414	moon
1275		1201	N-O
		1876	NO
1019	1018	10/0	110
1025	1025	1025	
1925	1925	1933	CO
2140	2140	2142	C0
2140	2140	2157	
0000	0000	2238	N2U HOON DOON
2288	2288	2295	HUCN, DUCN
	2030		DUCN
3132			NH
3572	3573		HOCN

¹⁷ D. E. Milligan and M. E. Jacox (unpublished data).

nent than in studies of the mercury arc photolysis of Ar:HNCO samples. The 2140-2146-cm⁻¹ absorption of CO is readily recognized in the present experiments, and a weak feature appearing in some experiments at 3132 cm⁻¹ may be assigned to the NH free radical.¹⁸ On subsequent mercury arc photolysis, features assigned to NO and to HOCN remain unchanged, but the prominent CO features grow somewhat. Unassigned features also appear at 484, 487, 541, 1275, 1918, and 1925 cm⁻¹. In Ar: HNCO experiments with approximately 50% deuterium enrichment, DOCN is also identified, but, within experimental error, the frequencies of the unassigned features remain unshifted, suggesting that they are not contributed by a hydrogencontaining species. All of these unassigned features diminish in intensity when the sample is subjected to mercury arc irradiation, as do the features assigned to NCO in the ultraviolet observations. The relative intensities of these features and their susceptibility to mercury arc photolysis are illustrated in Fig. 2. The 1275-cm⁻¹ feature, for which the ordinate scale has been expanded fourfold, is very weak, accounting for the failure to detect it in the deuterium-enrichment experiments. In N₂ matrix experiments, some NO and N₂O are also identified, and the 1918–1925-cm⁻¹ doublet is replaced by a single feature at 1935 cm^{-1} .

Vacuum-Ultraviolet Photolysis of HN₃ in CO

To obtain further isotopic data on the features tentatively assigned to NCO, it has been necessary to study the vacuum-ultraviolet photolysis of the system CO:HN₃, found in the ultraviolet studies to provide an excellent source of NCO. As shown by the first column of Table IV, numerous new features are ob-



FIG. 2. Ar:HNCO=200, 14°K. 118 μ M HNCO, deposited over period of 248 min, with simultaneous photolysis by microwave discharge through H₂:He=1:9. ---, 60 min subsequent Hg photolysis.

¹⁸ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 41, 2838 (1964).

TABLE IV. Frequencies (cm^{-1}) of infrared absorptions appearing after vacuum-ultraviolet photolysis of isotopically substituted CO:HN₃ samples.

CO:HN₃	CO(51.6% ¹³ C):HN ₃	CO:H(15N14N ₂)	Assignment
	476	486.8 sh	
489	489	488.8	
	582		HN18CO
594	594	594	HNCO
810	809 br	808	HNCO
815		815	HNCO
	1085		H13CO
1092	1091	1092	HCO
	1100		
1107	1107	1107	
1155			H ₂ CO
		1272	¹⁵ N ¹⁴ NO
		1287	N ₂ O
	1658		-
	1700		H ₂ ¹³ CO
	1715		H ₂ ¹³ CO
1728	1729	1730	H ₂ ¹² CO
1738	1738	1739	H ₂ ¹² CO
	1821		H ¹³ CO
1833		1833	
		1844	15NO
	1847		
1861	1860	1861	H ¹² CO
1876		1876	14NO
	1885		
1892	1891	1892	
		1931	
1938	1937	1938	
2490	2490	2490	HCO
2798	2798		H ₂ CO
2850	2850		
2866	2866		H ₂ CO
3432	3432	3432	HNCO

served in such samples. Although HOCN is not recognized in the resulting spectra, the more prominent HNCO absorptions do appear. The occurrence of photolytic processes involving H-atom detachment is demonstrated by the presence of intense HCO absorptions¹⁹ at 1092, 1861, and 2490 cm⁻¹. On subsequent mercury arc photolysis, the HCO features diminish somewhat in intensity, and features assigned to H₂CO grow. The 661- and 2350-cm⁻¹ CO₂ absorptions, omitted from Table IV because of their presence in unphotolyzed samples, also are observed to grow in intensity, and a feature at 1892 $\rm cm^{-1}$ grows greatly in intensity. Features which diminish in intensity on mercury arc irradiation appear at 489, 1833, and 1938 cm⁻¹. The 1275-cm⁻¹ region is, unfortunately, obscured somewhat by residual HN₈ absorption.

Frequencies of features appearing in experiments employing $^{13}\mathrm{C}$ and $^{15}\mathrm{N}$ isotopic substitution are also

¹⁹ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 41, 3032 (1964).



FIG. 3. (a) CO:HN₃=200. 14°K. 79.7 μM HN₂, deposited over period of 228 min, with simultaneous photolysis by microwave discharge through H₂. ---, 128 min subsequent Hg photolysis. (b) CO:H(¹⁵N¹⁴N₂) (96.8%) = 200, 14°K. 156 μM HN₂, deposited over period of 367 min, with simultaneous photolysis by microwave discharge through H₂. (c) CO (51.6% ¹⁵C):HN₂=100, 14°K. 73.3 μM HN₃, deposited over period of 87 min, with simultaneous photolysis by microwave discharge through H₂.

included in Table IV, and spectral regions of particular interest in these experiments are shown in Fig. 3. In all of these spectra, the prominent 1861-cm⁻¹ absorption is recognized. The diminution in intensity of this feature and of the 489-, 1833-, and 1938-cm⁻¹ features on mercury arc irradiation is illustrated in the dotted trace of Fig. 3(a). The 1833-cm⁻¹ feature, previously observed in other systems in which HCO is produced but nitrogen is not present,²⁰ is found in independent experiments to be characteristic of the reaction of OH with CO and has been assigned to the COOH free radical.²¹ The mercury arc photolysis of COOH is also found to lead to an increase in the infrared absorptions of CO₂. The 489-cm⁻¹ feature exhibits a partially resolved shoulder at about 487 cm⁻¹ in the ¹⁵N-substitution experiment. In the ¹³C-substitution experiment, features are observed at 476 and 489 cm⁻¹. Such behavior is appropriate to the bending mode of NCO; isotopic substitution at the central atom produces a much greater shift in the bending vibration of a linear triatomic species than does substitution at one of the end atoms. The 1938-cm⁻¹ feature has one counterpart of approximately equal intensity at 1931 cm⁻¹ in the ¹⁵N-substitution experiment. Its equally intense counterpart appears at 1885 cm⁻¹ in the ¹³C-substitution experiment. Thus, the isotopic substitution behavior of this feature is also consistent with its assignment to NCO.

A few other features in the CO:HN₃ experiments remain unassigned or may be only tentatively assigned.

The most prominent of these is the absorption at 1892 cm⁻¹, which grows more dramatically than any other feature on mercury arc photolysis. Independent experiments on the vacuum-ultraviolet photolysis of the system CO:HCN show, in addition to features characteristic of HCO, a prominent absorption at 1892 cm⁻¹, suggesting that this feature may be contributed by a product of the reaction of CN with CO. The 1876-cm⁻¹ feature and, in the ¹⁵N-substitution experiment, a feature of comparable intensity at 1844 cm⁻¹ are assigned to a relatively small amount of NO produced in these experiments. A rather prominent 1658-cm⁻¹ feature in the CO (51.6% ¹³C):HN₃ experiment is observed to diminish in intensity on mercury arc photolysis. Since this feature does not appear in any of the other experiments, further discussion is precluded. The remaining unassigned features are, in general, weak.

C+NO Studies

In Ar:NO+Ar:N₃CN experiments, features characteristic of the presence of NO appear after mercury photolysis at 487, 587, 809, 1281-1288, 1500, 1613, 1758, 1929, 2140, and 2235 cm⁻¹. The 587-, 1281-1288-, and 2235-cm⁻¹ features are readily recognized as arising from N₂O, and the 1613-cm⁻¹ feature is assigned to NO₂. The 1758-cm⁻¹ feature also appears when Ar: NO samples are subjected to mercury arc irradiation. Since it is not contributed by a carbon-containing species, it will not receive further discussion. The 2140-cm⁻¹ feature is assigned to CO. The remaining features are separated into two groups: the 487- and 1929-cm⁻¹ features, which diminish slightly in intensity when the sample is subjected to further mercury arc irradiation after complete photolysis of the N₃CN and NCN, and the 809- and 1500-cm⁻¹ features, which are relatively broad and which have no counterparts in the other systems discussed. The 809-cm⁻¹ feature is split into an 800-809-cm⁻¹ doublet in experiments employing $N_3^{13}CN$ (50%), but the 1500-cm⁻¹ feature remains unchanged. Without further data, an assignment of these features is not attempted.

On the other hand, it is possible to relate the 487and 1929-cm⁻¹ features to features tentatively assigned to NCO in experiments already described. In the ¹³C-substitution experiments, the 487-cm⁻¹ feature possesses an equally intense counterpart at 474 cm⁻¹; the 13-cm⁻¹ isotopic shift is equal to that observed for the comparable feature in the CO(51.6% ¹³C):HN₃ experiment. Unfortunately, the ¹³C counterpart of the 1929-cm⁻¹ feature apparently is obscured by the intense NO absorption near 1875 cm⁻¹ in the Ar:NO+ Ar: $N_3^{13}CN$ experiments. However, when an N_2 matrix is employed, a 476-489-cm⁻¹ doublet appears, and features are observed at 1883 and 1936 cm⁻¹. The 1936-cm⁻¹ feature coincides within experimental error with the 1935-cm⁻¹ feature of the N₂:HNCO experiments, and the 53-cm⁻¹ isotopic shift on ¹³C substitution

²⁰ M. E. Jacox and D. E. Milligan, J. Chem. Phys. 43, 866 (1956).

 $^{{}^{(150)}}_{21}$ D. E. Milligan and M. E. Jacox, "Matrix-Isolation Study of the Reaction of OH with CO. Infrared Spectrum of the COOH Free Radical," (to be published).

agrees well with the 52-cm⁻¹ shift obtained for the corresponding feature in the $CO(51.6\% \ ^{13}C)$:HN₃ experiment. The cyanogen azide experiments, unfortunately, do not provide a satisfactory system for further study of the isotopic substitution behavior of the 1275-cm⁻¹ feature. In most experiments, residual N₃CN absorption near 1263 cm⁻¹ complicates observations in this region, as do N₂O and CNN product absorptions.

The absorptions attributed tentatively to NCO in the 485-490- and 1915-1940-cm⁻¹ spectral regions disappear readily at temperatures above about 30°K, as molecular diffusion processes become important in the matrix. Such behavior is, of course, appropriate to a reactive species.

O+CN Study

In an experiment involving the vacuum-ultraviolet photolysis of an Ar:HC¹⁵N(95%):N₂O=200:1:1 sample, weak features are observed at 486, 1911, and 1919 cm⁻¹, in addition to features attributable to H¹⁵NC, to ¹⁵NO(1841 cm⁻¹), and to a small concentration of HNCO. The 486-cm⁻¹ feature agrees reasonably well with the frequency value previously postulated for ¹⁵NCO, and the 1911–1919-cm⁻¹ doublet is shifted 7 cm⁻¹ downward from the 1918–1925-cm⁻¹ doublet attributed to ¹⁴NCO in the Ar:HNCO experiments, the same isotopic shift recorded in the CO:H(¹⁵N¹⁴N₂) experiment.

DISCUSSION

Identification and Properties of NCO

Both chemically and spectroscopically, the simplest system in which NCO has been identified is Ar: HNCO, subjected to vacuum-ultraviolet photolysis. The ultraviolet observations have demonstrated the presence of a small concentration of NH, OH, and CN and of appreciable NCO in this system, and the infrared observations indicate that HOCN, NH, CO, and a species of photolytic behavior similar to that of NCO are present. It is inferred that the 484–487-, 1275-, and 1918-1925-cm⁻¹ absorptions are contributed by the free radical NCO. In the other systems a variety of products, some of them incompletely characterized, are observed, but, with allowance for matrix shifts, the 487- and 1918-1925-cm⁻¹ features are common to all of the systems studied, offering further support for their identification with NCO and affording the possibility of isotopic substitution studies.

The 1918–1925-cm⁻¹ feature of the Ar matrix experiments is replaced by a single feature at 1935 cm⁻¹ in N₂ matrix experiments and by a feature at 1938 cm⁻¹ in CO matrix experiments. Similar behavior has been observed for the highest-frequency fundamental of CCO, which appears at 1978 cm⁻¹ in an Ar matrix, at 1987 cm⁻¹ in an N₂ matrix, and at 1989 cm⁻¹ in a CO matrix.9 The frequency correspondence between the features assigned to N¹²CO in the N₂:NO+N₂:N₃¹³CN (50%) experiment and those assigned to NCO in the N₂:HNCO experiments is within experimental error. In the $Ar:NO+Ar:N_3CN$ experiment, only a single peak at 1929 cm⁻¹ may be assigned to NCO. Since two N_2 molecules are produced for each C atom in this system, it is not surprising that a value intermediate between that for NCO completely surrounded by Ar and that for NCO completely surrounded by N₂ is observed. The doubling of the two more prominent NCO fundamentals in the Ar matrix experiments may be related to the existence of more than one site for NCO isolated in this matrix; the broad absorption centered at 21 957 cm⁻¹ in the Ar matrix experiments and not fitting into the assignment scheme for the $A(2\Sigma^{+})-X(2\Pi)$ transition may, similarly, result from the $0,0^{\circ},0 - 0,0^{\circ},0$ band of NCO trapped in a second site or group of sites.

Dixon¹ has noted that there is an appreciable Renner effect for NCO in its ground electronic state, leading to the appearance of a 0,1°,0 ${}^{2}\Sigma^{+}$ vibrational level of NCO 441.4 cm⁻¹ above the ground-state zero vibrational level, of a 0,1²,0 $^{2}\Delta_{i}$ level 533.6 cm⁻¹ above the zero level, and of a 0,1°,0 $^{2}\Sigma^{-}$ level 637.4 cm⁻¹ above the zero level. In addition to the Renner splittings of the first vibrational level, NCO $X({}^{2}\Pi_{i})$ has an exceptionally large spin splitting, A = -95.6 cm⁻¹. Since this splitting is sufficiently great that, in the presence of paramagnetic impurities, the ${}^{2}\Pi_{1/2}$ level would be expected to be thermally depopulated at 14°K, the lowest-frequency infrared absorption, corresponding to the 0,1°,0 ${}^{2}\Sigma^{+}$ - 0,0¹,0 ${}^{2}\Pi_{3/2}$ vibrational transition, might be expected to appear at approximately 441.4 - (-95.6/2) =489.2 cm⁻¹, in excellent agreement with the 487-cm⁻¹ absorption observed for NCO in an Ar matrix. The spin splittings of the ${}^{2}\Sigma^{+}$ and ${}^{2}\Sigma^{-}$ states of the 0, 1°, 0 vibrational state are negligible, and a splitting comparable to that between the ${}^{2}\Pi_{i}$ levels of the 0, 0¹, 0 vibrational state occurs between the ${}^{2}\Delta_{3/2}$ and ${}^{2}\Delta_{5/2}$ levels of the 0, 1º, 0 vibrational state. Accordingly, transitions from the 0, 0¹, 0 ${}^{2}\Pi_{3/2}$ state to the 0, 1⁰, 0 ${}^{2}\Delta_{5/2}$, ${}^{2}\Delta_{3/2}$, and ${}^{2}\Sigma^{-1}$ states should result in infrared absorptions near 533.6, 629.2, and 685.2 cm⁻¹, respectively. Except that in some Ar:HNCO experiments a weak, broad feature of photolytic behavior similar to that of NCO appears near 540 cm⁻¹, no absorptions attributable to these other transitions have been observed. Although the frequency correspondence between the 540-cm⁻¹ infrared absorption and the predicted transition to the 0, 1°, 0 $^{2}\Delta_{5/2}$ vibrational state at 533.6 cm⁻¹ is reasonable, this assignment is not regarded as definitive.

Since it has been possible to assign all three fundamentals of NCO in the Ar matrix experiments, and since the behavior of the ν_2 and ν_3 vibrational fundamentals of NCO has been ascertained for both ¹³C and ¹⁵N substitution, it is possible to derive all of the force constants for this species. Vibrational frequencies

TABLE V. "Best-fit" force constants for NCO.

$(\nu_1 = 1275 \text{ cm}^{-1})$	$\nu_2 = 487 \text{ cm}^{-1}$,	$\nu_3 = 1922 \text{ cm}^{-1}$				
$F_{\rm CO}$	$= 12.93 \pm 0.3 \text{ md}$	yn/Å				
$F_{\rm CN}$	$F_{\rm CN} = 10.82 \pm 0.2 {\rm mdyn/\AA}$					
F_{CN-CO}	$=2.56\pm0.04$ md	yn/Å				
F _{NCO}	=0.434 mdyn•Å					

observed in the Ar matrix experiments most likely fall closest to the gas-phase values; relatively smaller matrix shifts are observed for both of the ultraviolet band systems of NCO in the Ar matrix studies than in N₂ and CO matrix studies. Therefore, frequencies observed in the Ar:HNCO system, which has the additional advantage of affording a value for v_1 , have been chosen for the calculation of force constants. The frequency of the more prominent feature associated with ν_2 , 487 cm⁻¹, is chosen as the value for the bending fundamental. Since the 1918- and 1925-cm⁻¹ features are approximately equally intense, an intermediate value, 1922 cm⁻¹, is chosen for ν_3 . Using these values for the fundamental frequencies of NCO and regarding the stretching interaction force constant as a parameter, it is possible to obtain real solutions for the two stretching force constants if $F_{CN-CO} \ge 2.499 \text{ mdyn/Å}$. The closest fit to the observed isotopic shifts in ν_3 is obtained for the set of force constants given in Table V. The isotopic shifts calculated for this set are compared with the observed values in Table VI. In this choice of force constants, it is noted that $\Delta \nu_8$ for ¹⁵N isotopic substitution has been determined with an accuracy of ± 1 cm⁻¹. $\Delta \nu_8$ for ¹³C isotopic substitution is subject to a somewhat greater experimental error. The 53-cm⁻¹ value observed in the N₂:NO+N₂:N₃¹³CN (50%) experiment agrees very well with the calculated shift. With the assumption of appropriate bond lengths, it is possible to obtain a unique solution for the bending force constant, $F_{\rm NCO}$. For the calculations of Tables V and VI, $r_{\rm NC}$ has been taken as 1.23 Å, the value obtained by Herzberg and Travis²² for the carbon-nitrogen bond length in NCN, and $r_{\rm CO}$ has been taken as 1.18 Å, to give a total molecular length of 2.41 Å, the upper bound to the molecular length of NCO obtained by Dixon.¹ Using these values, the agreement between the observed and calculated shifts for ν_2 on isotopic substitution is seen to be well within the experimental error.

The agreement between observed and calculated isotopic shifts shown in Table VI is certainly consistent with the assignment of the observed infrared features to a linear NCO structure. In accord with the conclusion of Dixon,¹ it appears likely that the CO bond of NCO in its ground state is somewhat stronger than the CN bond. The relatively large positive value of the stretching interaction force constant indicates that as one of the bonds is stretched the other is strengthened.²³

Reactions Occurring in the Matrix

Photolysis of HNCO by vacuum-ultraviolet radiation may occur either by the detachment of a H atom,

$$HNCO+h\nu \rightarrow H+NCO, \qquad (1)$$

or by photoisomerization to HOCN, which may then photolyze to produce NCO:

$$HNCO+h\nu \rightarrow NH+CO,$$
 (2)

$$NH+CO\rightarrow HOCN$$
, (3)

$$HOCN + h\nu \rightarrow H + NCO. \tag{4}$$

Reactions (2) and (3) have already been shown to occur upon photolysis of matrix-isolated HNCO with radiation from a medium-pressure mercury arc.³ Present data do not permit a distinction between these two processes. It is, however, pertinent to note that recent studies in our laboratory²⁴ of the vacuum-ultraviolet photolysis of the isoelectronic species HN₃ have shown that, while NH+N₂ constitute by far the major products in mercury arc photolysis studies, a strong absorption due to N₈²⁵ appears at 2720 A when vacuum-ultraviolet radiation is employed. In the HN3 photolysis, Reaction (4) becomes equivalent to Reaction (1).

It is noteworthy that the small concentration of NH observed in Ar: HNCO experiments probably does not arise from Reaction (2), since diatomic species generally are not found to diffuse in Ar matrices at 14°K. Quite possibly this NH is formed at sites removed from CO molecules by the reaction of N and H atoms which may be produced during the vacuum-ultraviolet photolysis and which are free to diffuse through the Ar matrix.

Processes leading to the formation of NCO in the CO:HN₃ experiments are probably closely related to

TABLE VI. Isotopic shifts (cm^{-1}) observed for NCO compared to those calculated using "best-fit" force constants.

	14	¹⁴ N ¹³ C ¹⁶ O		¹⁵ N ¹² C ¹⁶ O		
	Obs	Calc	Obs	Calc		
Δν1	•••	0.1±0.1	•••	24.2=0.5		
$\Delta \nu_2$	13	13.6	2.0	2.4		
$\Delta \nu_3$	52	53.4 ∓0.1	7	6.9∓0.8		

²³ J. W. Linnett and M. F. Hoare, Trans. Faraday Soc. 45, 844 (1949).
²⁴ D. E. Milligan and M. E. Jacox (unpublished data).
²⁵ A. E. Douglas and W. J. Jones, Can. J. Phys. 43, 2216

(1965).

²² G. Herzberg and D. N. Travis, Can. J. Phys. 42, 1658 (1964).

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those involved in the HNCO photolysis studies, with the addition of the reactions involved in the initial formation of HNCO:

$$HN_{3}+h\nu \rightarrow NH+N_{2}, \tag{5}$$

$$\mathbf{NH} + \mathbf{CO} \rightarrow \mathbf{HNCO}. \tag{6}$$

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Other processes involving initial formation of N₃ may also contribute to the production of NCO.

In the Ar:NO+Ar:N₈CN studies, the sequence of possible reactions becomes very complex, since associated species of NO are known to photolyze upon being subjected to mercury arc irradiation and since the reactive species NCN and CNN are also produced. Accordingly, a complete assignment of the product absorptions has not heretofore been possible. The studies are, however, significant, since C atoms are known to be produced in this system and since a reasonable concentration of NCO is identified among the reaction products. Stabilization of NCO may result either from the photoisomerization of initially formed CNO or from the rearrangement of a cyclic intermediate.

Similarly, in the studies of the vacuum-ultraviolet photolysis of Ar:HCN:N₂O samples, CNO is not detected, whereas NCO is. However, the formation of NCO by the reaction of O atoms with CN would not necessarily involve rearrangement of an intermediate species. It is, unfortunately, not possible to determine the extent of contribution of the reaction

$$HCN+O \rightarrow HNCO$$
 (7)

to the final yield of NCO in this system.

Photolysis of NCO

The diffuseness of several of the bands assigned by Dixon² to the $B({}^{2}\Pi)-X({}^{2}\Pi)$ transition of NCO led him to suggest that either NCO is predissociated in the upper state of this transition or the $B({}^{2}\Pi)$ state of NCO is perturbed, resulting in unresolved groups of lines. The occurrence of predissociation in the spectral region of interest has been confirmed by the present observations. Several considerations point to the occurrence of the process

$$NCO+h\nu(2537 \text{ \AA}) \rightarrow N+CO.$$
 (8)

Most significantly, in the Ar: HNCO system, chemically the simplest system studied, the ultraviolet absorption of CN remains unchanged upon photolysis of NCO, whereas the infrared absorption of CO, already prominent, is observed to grow in intensity as NCO is photolyzed. Energetic considerations would also appear to favor somewhat the formation of N+CO, rather than of O+CN, under these conditions. As shown by Table_VII, in which the zero of the energy scale corresponds to the production of N+CO in their ground states, processes leading to the production of CO $X({}^{1}\Sigma^{+})$ and either N (${}^{4}S_{u}$) or N (${}^{2}D_{u}$) may occur at lower energies than the photoproduction of O (${}^{3}P_{g}$) + CN $X({}^{2}\Sigma^{+})$. Whether 2537-Å radiation would suffice to produce these latter products is, of course, dependent upon the dissociation energy of NCO, which, unfortunately, is not known.

The growth in absorptions assigned to CO₂ and, tentatively, to CNCO when photolyzed CO:HN₃ samples are subjected to mercury arc irradiation might, at first glance, be taken as support for the photodissociation of NCO into O (${}^{3}P_{o}$) + CN X(${}^{2}\Sigma^{+}$). It should, however, be noted that such alternative processes as

$$NCO^* + CO \rightarrow CO_2 + CN$$
 (9)

may lead to the growth in the concentration of these species. Thus, it is concluded that the observation of enhanced CO and CNCO absorptions following mercury arc irradiation of the photolyzed CO: HN_3 samples is not inconsistent with the primary photodecomposition of NCO into N+CO, indicated by studies of the chemically simpler Ar:HNCO system.

It is, finally, interesting to note that NCO isolated in a CO matrix photolyzes at a rate comparable to that observed in the other matrices. This observation would, of course, be anticipated if Reaction (9) were to play a significant role. Alternatively, failure to observe an enhanced photolytic stability of NCO in a CO matrix may indicate either that initially formed N (${}^{4}S_{u}$) does not react with CO to form a stable NCO ${}^{4}\Sigma^{-}$ species or that there is an appreciable activation energy for the recombination of N (${}^{2}D_{u}$) with CO.

CONCLUSIONS

The three vibrational fundamentals of the free radical NCO have been identified at 487, 1275, and 1922 cm⁻¹ in studies of the vacuum-ultraviolet photolysis of Ar: HNCO samples at 14°K. Ultraviolet studies of this system confirm the presence of NCO. Observations of the $B(2\Pi)-X(2\Pi)$ absorption system of NCO have been extended to shorter wavelengths than previ-

TABLE VII. Relative energies required for production of various dissociation products of NCO.•

NCO states	Dissociation products	cm ^{−1}
4 <u>Σ</u>	$N(^{4}S_{\mu}) + CO X(^{1}\Sigma^{+})$	0
${}^{2}\Sigma^{-}, X({}^{2}\Pi), {}^{2}\Delta$	$N(^{2}D_{y}) + CO X(^{1}\Sigma^{+})$	19 200
${}^{2}\Sigma^{-}, X({}^{2}\Pi),$	$O(^{3}P_{q}) + CN X(^{2}\Sigma^{+})$	24 200
⁴ Σ [−] , ⁴ Π		
$A(^{2}\Sigma^{+}), B(^{2}\Pi)$	$N(^{2}P_{u}) + CO X(^{1}\Sigma^{+})$	28 800
$A(^{2}\Sigma^{+}), ^{2}\Sigma^{-},$	$O(^{3}P_{q}) + CN A(^{2}\Pi)$	33 500
$B(^{2}\Pi), ^{2}\Delta, ^{4}\Sigma^{+},$		
$4\Sigma^{-}, 4\Pi, 4\Delta$		

^a Reference 1.

ously reported. Isotopic substitution studies indicate that the carbon-oxygen bond of ground-state NCO is most likely somewhat stronger than the carbon-nitrogen bond. There is an appreciable positive stretching interaction force constant. In supplementary studies,

evidence is obtained for the reaction of C atoms with NO and of O atoms with CN, leading to the stabilization of NCO, but not of a detectable concentration of CNO. When subjected to radiation of wavelength near 2537 Å, NCO photolyzes, producing N atoms and CO.

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Dependence of Correlation Energy upon Bond Angle: Investigation of Interactions between **Nearly Degenerate Electronic Configurations***

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Configuration interaction of low-lying electronic states is used to investigate the molecular correlation energy as a function of bond angle. Qualitative aspects of the problem are discussed using the molecularorbital diagrams of Walsh and Mulliken. Results of configuration-interaction calculations of BeH2 and NO2+ are reported. The possibility of double minima in the potential surfaces for AB2 molecules is considered.

I. INTRODUCTION

It is well known that molecular-orbital wavefunctions, in general, fail to give quantitatively meaningful potential-energy surfaces. The difference between the energy of the Hartree-Fock or best molecular-orbital wavefunction and the exact nonrelativistic energy is often referred to as the correlation energy. There are many cases known for which the correlation energy varies as a function of bond length,¹ but there is very little information on whether the correlation energy changes with bond angle. One reason for this is the scarcity of experimental information concerning the nature of the potential-energy surface even for the simplest polyatomic molecules. Bond angles and force constants are known for many polyatomic species,² but it is difficult to obtain the potential-energy surface for bond-angle changes from this information because, unlike changes in bond length where the correct dissociation products are well characterized, for changes in bond angle the correct limiting behavior is not known. Another reason for the lack of information concerning the dependence of the correlation energy upon bond angle is that direct calculation of the total correlation energy for a polyatomic molecule is a formidable task and has been achieved only for the simplest polyatomic molecules.8 Recently there have been a number of *ab initio* calculations of potential-energy surfaces for polyatomic molecules. Many of these studies⁴⁻⁹ have been carried out within the molecular-orbital approximation. In all of these cases fairly good bond angles were reported. This may indicate that the correlation energy does not change significantly with bond angle. We believe this question to be an open one and in this paper we hope to provide some additional insight into this problem.

II. GENERAL CONSIDERATIONS

In principle the exact nonrelativistic wavefunction Ψ may be expanded as a linear combination,

$$\Psi = \sum_{i} C_{i} \Phi_{i}, \qquad (1)$$

where the configurations Φ_i are antisymmetric products of molecular spin-orbitals. The Hartree-Fock or best molecular-orbital wavefunction is just a single configu-

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[†] AFOSR Postdoctoral Fellow 1967–1968. [†] The classic example is that of the hydrogen molecule; in this case the Hartree-Fock wavefunction does not dissociate correctly. ² G. Herzberg, *Molecular Spectra and Molecular Structure*. *III*. Electronic Spectra and Electronic Structure of Polyatomic Molecules (D. Van Nostrand Co., Inc., Princeton, N.J., 1966).

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