oven. This technique prevents condensation of sample in the analyzer chamber, and thus possible deterioration of electron focussing is avoided. Most of the binding energies are based on spectrometer calibrations with the N_2 1s, Ne 1s, and Ne 2s lines. However, in the case of the O 1s and N 1s spectra of $CpCr(NO)_2NO_2$, it was possible to measure the binding energies relative to the decomposition product nitric oxide, NO. In a separate run, we determined the binding energies of a commercial sample of nitric oxide (Matheson) as follows: E_B(O 1s) = 543.32 (6) eV (strong line), 544.13 (16) eV (weak line), 543.52 (8) eV (weighted average), fwhm(O 1s) = 1.06 (12) eV (strong line), 1.07 (33) eV (weak line); E_B(N 1s, deconvoluted strong line) = 410.32 (4) eV, fwhm(N 1s, deconvoluted strong line) = 1.29 (12) eV; E_B(N 1s, deconvoluted weak line) = 411.68 (13) eV, fwhm(N 1s, deconvoluted weak line) = 1.40 (24) eV.

$CpCr(NO)_2NO_2$,[15] $CpW(NO)_2H$,[8] $CpM(CO)_2NO$,[16] and $CpM(NO)_2Cl$[16] (M = Cr, Mo, W) were prepared according to published procedures.

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Registry No. $CpCr(CO)_2NO$, 36312-04-6; $CpCr(NO)_2NO_2$, 68013-60-5; $CpCr(NO)_2Cl$, 12071-51-1; $CpMo(CO)_2NO$, 12128-13-1; $CpMo(NO)_2Cl$, 12305-00-9; $CpW(CO)_2NO$, 12128-14-2; $CpW(NO)_2H$, 69532-01-0; $CpW(NO)_2Cl$, 53419-14-0.

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Metal Vapor–Acetylene Cryochemistry: Vibrational, Optical, and SCF-Xα-SW Investigations of $M(\pi\text{-}C_2H_2)_n$ (Where M = Ni or Cu; n = 1 or 2). Comparison with Chemisorbed Acetylene

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Nickel and copper vapor cocondensation reactions, with pure acetylene and acetylene/inert gas matrices, have been investigated over a range of temperatures upward from 10–12 K, by infrared and ultraviolet–visible spectroscopy. A combination of ligand concentration, bulk thermal annealing, and mixed isotopic $^{12}C_2H_2/^{13}C_2H_2$ substitution experiments under mononuclear reaction conditions established the existence of two acetylene complexes of the type $M(C_2H_2)_n$ (where M = Cu or Ni, n = 1 or 2). The vibrational data favored simple π-acetylene bonding in all cases, thereby supporting the conclusions drawn from recent ESR observations for the copper–acetylene system. Thermal stability studies in solid acetylene established decomposition temperatures around 150 and 80 K for the $Ni(C_2H_2)_2$ and $Cu(C_2H_2)_2$ species, respectively, following the similar order observed for $Ni(C_2H_4)_3$ and $Cu(C_2H_4)_3$ and paralleling the trend observed for acetylene chemisorbed on Ni and Cu surfaces. The optical spectroscopic properties and bonding schemes for the $M(C_2H_2)$ complexes were probed by the SCF-Xα-SW molecular orbital method. A Dewar–Chatt–Duncanson bonding picture emerged for both complexes but with minimal π delocalization of charge from the metal to the ligand for $Cu(C_2H_2)$. A $^2A_1$ electronic ground state configuration was predicted for $Cu(C_2H_2)$, which was in agreement with predictions based on an analysis of ESR data. Calculated electronic properties and optical trends were found to be well represented for $Cu(C_2H_2)$ and $Ni(C_2H_2)$ and proved to be helpful in discussing the interrelationships between the acetylene data and the corresponding ethylene data. The various modes of bonding observed for chemisorbed acetylene were briefly surveyed, and, in the case of $Ni(C_2H_2)$, the problems inherent in localized bonding discussions of chemisorbed acetylene were examined in light of recent high-resolution electron energy loss spectroscopy studies of the extensively rehybridized, di-σ form of acetylene on metal surfaces.

Introduction

The determination of the molecular geometry and electronic structure of hydrocarbon molecules adsorbed on transition-metal surfaces is a problem of central concern to those involved in unravelling fundamental processes in heterogeneous catalysis. Information of this kind may not only reveal details of the nature and strength of the chemisorption bond but may also provide an insight into surface-molecule transformations and surface-catalyzed reactions.

The hydrocarbon chemisorption problem has been probed by both semiempirical and ab initio molecular orbital techniques using, for example, $M_n(C_2H_2)$ and $M_n(C_2H_4)$ localized bonding models in which the metal and metal cluster size are varied in an attempt to examine the convergence behavior of these finite molecular systems toward the corresponding bulk experimental and/or theoretical data.[2-14] With use of metal atom matrix spectroscopic methods, species such as $M_n(C_2H_4)$, where M = Co,[15] Ni[16b], or Cu[17] and n = 1 or 2, have recently

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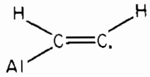
been synthesized and are proving to be of considerable value to σ/π discussions of chemisorbed ethylene on the respective bulk metals, as well as providing a valuable testing ground for various molecular orbital techniques.[2-14]

In view of the activity surrounding the problem of metal–acetylene surface species[18-22] and the relevance of the data to heterogeneous catalytic reactions involving alkynes, we have undertaken a program of research aimed at the spectroscopic characterization of $M_n(C_2H_2)$ chemisorption models. In the context of metal atom–alkyne matrix chemistry, Kasai[23] has recently reacted acetylene with copper atoms at 4.2 K and has demonstrated, by matrix ESR techniques, the existence of labile, binary $Cu(C_2H_2)_{1,2}$ π complexes, similar to the aluminum atom–ethylene product formulated as π-bonded $Al(C_2H_4)$[23b] but in sharp contrast to the aluminum atom–acetylene cocondensation product,[24] assigned to the radical species



The latter has been examined recently by ab initio techniques.[25]

On a macrosynthetic scale, Lagowski[26] has shown that nickel atoms react with methyl acetylene and 2-pentyne at −196 °C to yield various organic oligomers as well as a black nickel-containing species, which independently oligomerizes acetylene to form benzene and cyclooctatetraene. Interestingly, iron atoms were found to react with 2-pentyne to yield a symmetric tetramer as the sole hydrocarbon product.[26] An early published study from a Russian group[27] showed that Ni, Pd, and Pt vapors react with *n*-butylacetylene and propargyl chloride to produce π complexes of undetermined stoichiometry. Recently, Klabunde[28] found that Ni or Pd atoms reacted at 77 K with an excess of hexafluoro-2-butyne (HFB) to yield labile $M(CO)_2(HFB)$ complexes in the presence of CO that spontaneously formed $M_4(CO)_4(HFB)_3$ cluster species similar to those synthesized by Stone and co-workers[29] from $Ni(CO)_4$–HFB reactions.

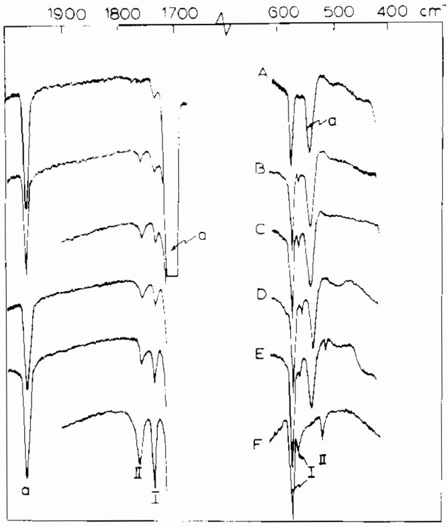


Figure 1. Matrix infrared spectra of the products formed from the reaction of Ni atoms with a $^{12}C_2H_2/Kr = 1/10$ gas mixture, on deposition at (A) 15 K and after warm-up to (B) 30 K, (C) 35 K, (D) 40 K, (E) 45 K, and (F) 55 K. ($a = {}^{12}C_2H_2$, $I = Ni({}^{12}C_2H_2)$, $II = Ni({}^{12}C_2H_2)_2$). Note that the complete region of the infrared spectrum, 4000–200 cm^{-1}, was scanned in all experiments. However, only selected regions of the spectra are illustrated in Figures 1–4.

Table I. Vibrational Spectra of C_2H_2 in Various Matrices[a]

$^{12}C_2H_2$ (pure)	$^{12}C_2H_2$/ Ar = 1/10	$^{12}C_2H_2$/ Kr = 1/10	$^{13}C_2H_2$/ Ar = 1/20	$^{12}C_2H_2$ (gas)[b]	assignt
3220	3240	3240	3225	3287	ν_1(C–H)
1958	1974	1974	1902	1956	$2\nu_4 + \nu_5$
1690	1704	1705	1615		*c*
1400	1360	1360	1346	1328	$\nu_4 + \nu_5$
1234	1250	1230	1250		*c*
760	764	762	750	729	$\nu_5(\delta(H–C–H))$

[a] Frequencies in cm^{-1}. [b] Values taken from G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. II, Van Nostrand, Princeton, N.J., 1945. [c] Probably associated with acetylene multimers, analogous to those recently observed in concentrated ethylene/inert gas matrices (see E. Rytter and D. M. Gruen, *Spectrochim. Acta, Part A*, 35A, 199 (1979)).

In this first report, we have focussed our attention on nickel and copper atom–acetylene cryochemical reactions, exclusively under mononuclear conditions, and find that binary acetylene complexes of the form $M(C_2H_2)$ and $M(C_2H_2)_2$ are the sole products for both metals. In what follows, the infrared, optical, and SCF–Xα–SW characterization of these complexes will be presented.

Experimental and Theoretical Techniques

Monatomic Ni and Cu vapors were generated by directly heating a 0.020-in. ribbon filament of the metal, in the case of Ni, and a tungsten-rod assembly around which copper wire was wrapped, with ac in a vacuum furnace similar to that described previously.[30] The nickel and copper metal (99.999%) was supplied by McKay, New York. Research grade $^{12}C_2H_2$ (99.999%), Ar (99.999%), and Kr (99.999%) were supplied by Matheson of Canada and $^{13}C_2H_2$ (91%) by Stohler Isotopes, Montreal. The rate of metal atom deposition was continuously monitored with use of an in situ quartz-crystal microbalance assembly.[31]

In the infrared experiments, matrices were deposited onto a CsI optical window cooled to 10–12 K by means of an Air Products Displex closed-cycle helium refrigerator. Infrared spectra were recorded on

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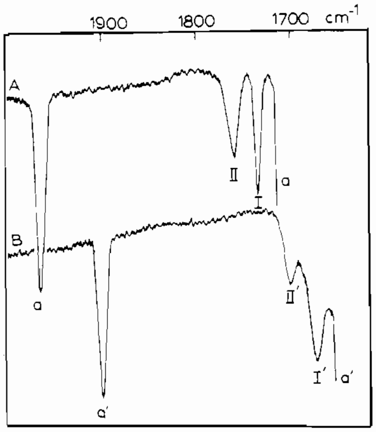

Figure 2. Matrix infrared spectra observed on cocondensing Ni atoms with (A) $^{12}C_2H_2/Kr = 1/10$ and (B) $^{13}C_2H_2/Kr = 1/10$ gas mixtures (a = $^{12}C_2H_2$, a′ = $^{13}C_2H_2$, I = $Ni(^{12}C_2H_2)$, I′ = $Ni(^{13}C_2H_2)$, II = $Ni(^{12}C_2H_2)_2$, II′ = $Ni(^{13}C_2H_2)_2$).

a Perkin-Elmer 180 spectrophotometer. Ultraviolet-visible spectra were recorded on a standard Varian Techtron instrument in the range 190–900 nm, the sample being deposited onto a NaCl optical window.

Theoretical calculations were performed within the framework of the self-consistent field–Xα–scattered wave method,[32] with use of a modified version of the computer programs originally developed by Johnson and Smith. Details of the methodology have been previously specified.[33] Distances and coordinates are expressed as multiples of the Bohr radius of the hydrogen atom (0.529 177 06 (44) Å) and energies are given in terms of the Rydberg unit (1.097 373 177 (83) × 10^5 cm^{-1}, 13.605 804 (36) eV).

Infrared Studies

Nickel Atom–Acetylene Reactions. In the reaction of nickel atoms with acetylene, metal concentrations were maintained low enough to minimize effects due to nickel aggregation.[34,35] Similar metal to matrix ratios ($1/10^4$) had been used previously in the nickel–ethylene system[16b,36] to isolate three mononuclear species $Ni(C_2H_4)_n$, where n = 1–3. The results of ligand concentration and thermal annealing experiments in the nickel–acetylene system, under similar metal concentration conditions, showed the presence of only two binary nickel–acetylene species.

The existence of two distinct complexes was established from a study of a matrix formed from the cocondensation of Ni atoms and a $C_2H_2/Kr = 1/10$ gas mixture at 15 K. Following deposition (Figure 1A) the only features, other than those absorbances attributable to uncomplexed C_2H_2 in the matrix (listed in Table I and designated "a" in Figures 1–3), were weak spectral lines at 1730 and 570 cm^{-1} (species I). Upon warming of the matrix to 30 K, new spectral features appeared around 1760/1757 cm^{-1} (species II). Annealing the matrix to 55 K, in stages, permitted the differentiation of two distinct sets of absorbances, 1734, 572/556 cm^{-1} (species I) and 1757, 512 cm^{-1} (species II). Carbon–hydrogen stretching modes around 3130 cm^{-1} evidently overlapped for both species. An a priori assignment of the two products, based on this infrared data, could then be made as

$$I = Ni(C_2H_2) \qquad II = Ni(C_2H_2)_2$$

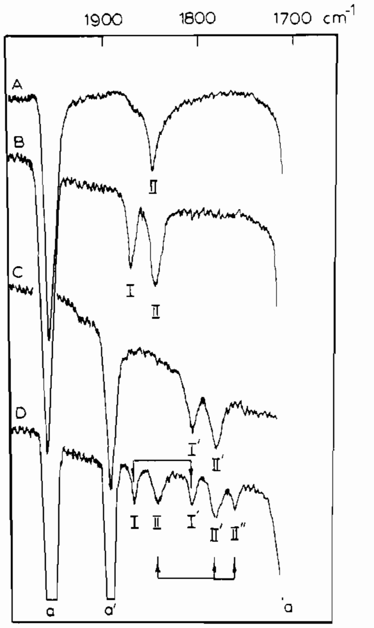

Figure 3. Matrix infrared spectra observed on cocondensing Cu atoms at 10–12 K with (A) $^{12}C_2H_2$, (B) $^{12}C_2H_2/Ar = 1/10$, (C) $^{13}C_2H_2/Ar = 1/10$, and (D) $^{12}C_2H_2/^{13}C_2H_2/Ar = 1/1/20$ gas mixtures (a = $^{12}C_2H_2$, a′ = $^{13}C_2H_2$, I = $Cu(^{12}C_2H_2)$, I′ = $Cu(^{13}C_2H_2)$, II = $Cu(^{12}C_2H_2)_2$, II′ = $Cu(^{13}C_2H_2)_2$, II″ = $Cu(^{12}C_2H_2)(^{13}C_2H_2)$).

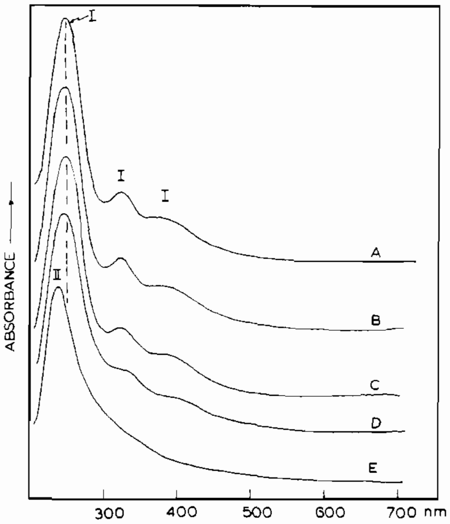

Figure 4. Matrix ultraviolet–visible spectra observed on cocondesing Ni atoms with $^{12}C_2H_2$ at (A) 10–12 K followed by warm-ups to (B) 25 K, (C) 40 K, (D) 55 K, and (E) 70 K. Note the small, but reproducible, shift in the high-energy band.

The formation of a less rigid matrix, from the cocondensation reaction of Ni atoms and a $C_2H_2/Ar = 1/10$ gas mixture at 15 K, resulted in the initial isolation of both species I and II, as shown by the presence of ν(C≡C) stretching modes at 1730 and 1760 cm^{-1}, respectively (both have undergone slight matrix-induced frequency shifts from their values found in the Kr matrix). However, codeposition of Ni atoms with pure C_2H_2 at 15–20 K resulted in the exclusive synthesis of species II, with ν(C≡C) modes at 1760/1756 cm^{-1} (matrix site splitting effect). When a similar experiment was performed at 10–12 K in pure C_2H_2, both species I and II could be isolated (recall that at 10–12 K in pure C_2H_4 both $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$ were isolated[36]). The above data clearly support the stoichiometric assignments mentioned earlier, with the lowest stoichiometry species $Ni(C_2H_2)$, as expected, being most evident in the more rigid Kr matrix. Additional support for these assignments was obtained from dilution experiments of C_2H_2 in Ar, where it was found that $Ni(C_2H_2)$ was preferentially isolated in $C_2H_2/Ar = 1/50$ matrices at low temper-

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Table II. Infrared Spectra for $Ni(C_2H_2)_n$ ($n = 1, 2$) in Argon and Krypton Matrices[a]

Ar (12K)	Kr (12 K)	assignt
3112[b]	3130	ν(C–H), I + II[c]
1760[d]	1757	ν(C≡C), II
1729	1734	ν(C≡C), I
570/560[e]	572/556	ν(Ni–C), I
	512	ν(Ni–C), II

[a] Frequencies in cm^{-1}. [b] Suspected band overlap of $Ni(C_2H_2)_{1,2}$ in ν(C–H) region. [c] I = $Ni(C_2H_2)$, II = $Ni(C_2H_2)_2$. [d] Matrix split ν(C≡C) at 1761/1757 cm^{-1} observed for $Ni(C_2H_2)_2$ in pure acetylene and dilute acetylene matrices at 12 K. [e] Matrix split ν(Ni–C) mode.

atures and the gradual appearance of absorbances associated with $Ni(C_2H_2)_2$ was observed upon annealing to 30–35 K.

Higher temperature depositions were also investigated in the Ni/C_2H_2 systems. At 77 K, under mononuclear nickel conditions and in pure acetylene, $Ni(C_2H_2)_2$ was exclusively generated, as shown by the single ν(C≡C) absorption at 1760 cm^{-1} (slightly broadened compared with that found in inert-gas matrices). Careful annealing experiments demonstrated that $Ni(C_2H_2)_2$ was thermally stable to at least 150 K. Matrix annealing experiments, with rare-gas supports, showed that $Ni(C_2H_2)$ existed as a discrete entity up to about 50 K. It may be noted that the high-temperature synthesis of $Ni(C_2H_2)_2$ under matrix conditions is analogous to the 77 K synthesis of $Ni(C_2H_4)_3$ from nickel vapor and ethylene.[36]

By reference to the vibrational data for a wide range of transition-metal alkyne complexes,[23b,37] band assignments (Table II) could be determined, with ν(C—H) around 3100 cm^{-1}, ν(C≡C) in the 1700–1770-cm^{-1} region, and ν(Ni—C) modes in the 500–560-cm^{-1} region. (The complete infrared spectral range, 4000–200 cm^{-1}, was scanned in each experiment, and at no time were absorptions observed which could be assigned to a σ-bonded acetylene species.) On the assumption that the vibrational assignments were reasonable, one could safely identify the $Ni(C_2H_2)_{1,2}$ species as simple π complexes, with the frequency of the ν(C≡C) mode of coordinated acetylene shifted about 250 cm^{-1} with respect to that of free acetylene (1974 cm^{-1}). This parallels the situation found for the $Ni(C_2H_4)_{1,2}$ complexes,[36] which showed shifts of roughly 150 cm^{-1} for coordinated ethylene, in line with the GVB–CI π-bonding description of $Ni(C_2H_4)$ and $Ni(C_2H_2)$[16] and the SCF-Xα–SW π-bonding picture of $M(C_2H_4)$[4,5,33] and $M(C_2H_2)$ for M = Ni or Cu (to be discussed later).

In principle mixed $^{12}C_2H_2/^{13}C_2H_2$ isotope substitution experiments should unequivocally establish the stoichiometries of the two proposed mononuclear complexes (see, for example, $^{12}C_2H_4/^{13}C_2H_4$ studies of $Pd(C_2H_4)_n$[38]). A ligand concentration study in $^{13}C_2H_2/Kr$ matrices indicated that the mode displaying the greatest carbon mass sensitivity was the ν(C≡C) stretching vibration. These experiments established ν(C≡C) for $Ni(^{13}C_2H_2)_{1,2}$ at 1668 and 1700 cm^{-1}, respectively (Figure 3). The red shifts of the absorptions of the $^{13}C_2H_2$ complexes relative to their $^{12}C_2H_2$ counterparts, roughly 60 cm^{-1}, were close to those predicted on the basis of a simple diatomic harmonic oscillator mass ratio relationship. (Note that the position of the II″ band below that of the II′ band in Figure 3D indicates that there must be *some* coupling between the two ligands of the bis(acetylene) complex.) Unfortunately, band overlap complications with uncomplexed $^{12}C_2H_2$ in a mixed $^{12}C_2H_2/^{13}C_2H_2/Kr$ experiment precluded a definite assignment of stoichiometry in the nickel system. However, since the ν(C≡C) modes of the Cu/C_2H_2 analogues were blue shifted relative to those of nickel (to be described), this isotope overlap problem was eliminated and the monoacetylene and bis(acetylene) formulations were clearly established. The close resemblance of the infrared spectra of the Ni- and Cu-acetylene matrix reaction products, together with Kasai's ESR-based (proton hyperfine) stoichiometric assignments for $Cu(C_2H_2)_2$,[23] points toward a $Ni(C_2H_2)_{1,2}$ formulation.

Table III. Infrared Spectra for $Cu(C_2H_2)_n$ ($n = 1, 2$)[a]

$Cu(C_2H_2)$[b]	$Cu(C_2H_2)_2$[b]	assignt
3040	2928	ν(C–H)
	2856	ν(C–H)
1870	1850	ν(C≡C)
380	520	ν(Cu–C)

[a] Frequencies in cm^{-1}. [b] Average values from various C_2H_2, C_2H_2/Ar matrices.

Copper Atom–Acetylene Reactions. As indicated above, the vibrational characteristics of the mononuclear copper–acetylene complexes were quite similar to those of the corresponding nickel species. For example, a codeposition of copper atoms and pure C_2H_2 gas ($1/10^4$) at 10–12 K resulted in the formation of a single species (Figure 3A), with infrared absorptions at 2928 and 2856 (ν(C—H)), 1850 (ν(C≡C)), and 420 cm^{-1} (ν(Cu—C)). Warming the matrix resulted simply in the sharpening and growth of these spectral features which, around 80 K, decayed to zero. When acetylene was diluted with argon (Figure 3B), a group of new bands was also observed, with frequencies around 3040 (ν(C—H)), 1870 (ν(C≡C)), and 380 cm^{-1} (ν(Cu—C)). The warm-up behavior of these new bands suggested that they were associated with a species of lower stoichiometry than that observed in pure C_2H_2 matrices. In this way, the complex absorbing at 1870 cm^{-1} was associated with $Cu(C_2H_2)$ (species I, corresponding to Kasai's species B[23]), while that absorbing at 1850 cm^{-1} was assigned to $Cu(C_2H_2)_2$ (species II, corresponding to Kasai's species C[23]). Vibrational spectra and assignments are summarized in Table III.

Confirmatory ^{13}C isotope substitution experiments supported these proposals. The most sensitive stoichiometric probe was the ν(C≡C) mode which displayed shifts on the order of 60 cm^{-1} on passing from the $^{12}C_2H_2$ to the $^{13}C_2H_2$ complexes (1812 and 1784 cm^{-1} for $Cu(^{13}C_2H_2)$ and $Cu(^{13}C_2H_2)_2$, respectively (Figure 3C)). The ν(C—H) vibrational modes showed little sensitivity to ^{13}C substitutions, which was not unexpected in view of the relatively pure nature of ν(C—H) stretching modes. Previous work[39] indicated that ν(C—H) modes were only slightly affected by ^{13}C substitution (e.g., the ν(C—H) modes of $Co_2(CO)_6(^{12}C_2H_2)$ shifted only 4 cm^{-1} when $^{12}C_2H_2$ was replaced by $^{12}CH^{13}CH$). Stoichiometries were assigned from $^{12}C_2H_2/^{13}C_2H_2/Ar$ mixed isotope experiments (Figure 3D), which showed an isotopic triplet at 1850, 1784, and 1760 cm^{-1} for species II, indicating a bis(acetylene) complex and an isotopic doublet at 1870 and 1812 cm^{-1} for species I, confirming the monoacetylene formulation.

A comparison of the vibrational data for the copper and nickel species revealed that there was a somewhat stronger interaction between the nickel and the acetylene ligand than between copper and acetylene. This was reflected in the smaller shift of the frequency of the ν(C≡C) mode on coordination of acetylene to copper (120 cm^{-1}), compared with that of nickel (250 cm^{-1}), for both the monoacetylene and bis(acetylene) complexes with a correspondingly higher ν(Ni—C) mode (570–512 cm^{-1}) than the ν(Cu—C) mode (420–350 cm^{-1}). The thermal stabilities of the complexes also reflected this trend in metal–ligand bond strengths, with $Ni(C_2H_2)_2$ being stable in solid C_2H_2 up to 150 K compared with $Cu(C_2H_2)_2$ which was stable only to 80 K (although the latter could be a manifestation of diffusion/aggregation phenomena of the type $Cu(C_2H_2)_2 \rightarrow Cu_2(C_2H_2)_n \rightarrow$ etc., similar to that observed in the Cu/C_2H_4 system[17]). Significantly, this thermal stability trend parallels that observed for the $Cu(C_2H_4)_n/Ni(C_2H_4)_n$ complexes.[17,36]

Optical Experiments

Nickel Atom–Acetylene Reactions. The optical spectra of $Ni(C_2H_2)_{1,2}$ were not entirely analogous to those of $Ni(C_2H_4)_{1,2,3}$[16b,36] although it was evident that in both cases zerovalent nickel π complexes had been created. In the ethylene case, only one ultraviolet absorption was observed per complex, with the absorption energies monotonically blue shifting with increasing olefin stoichiometry.[16b,36] In the nickel–acetylene species, on the other hand, more than one ultraviolet absorption could be associated with each complex.

Clear optical confirmation of the existence of two binary nickel–acetylene complexes stemmed from the codeposition of nickel atoms, under mononuclear conditions ($1/10^4$), with pure acetylene at 10–12 K. The spectrum on deposition displayed three distinct bands at 394, 328, and 256 nm. Annealing to 25, 40, 55, and 70 K (Figure 4) resulted in the decay of the two lowest energy absorptions with a small, but reproducible, shift of the high-energy band to 245 nm. The final

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(37) E. Maslowsky, Jr., "Vibrational Spectra of Organometallic Compounds", Wiley, New York, 1977.

(38) H. Huber, G. A. Ozin, and W. J. Power, *Inorg. Chem.*, **16**, 979 (1977).

(39) Y. Iwashita, F. Tamura, and A. Nakamura, *Inorg. Chem.*, **8**, 1179 (1969).

Table IV. Optical Spectra for $M(C_2H_2)_n$ (M = Ni, Cu; *n* = 1, 2)[a]

$Ni(C_2H_2)$	$Ni(C_2H_2)_2$	$Cu(C_2H_2)$	$Cu(C_2H_2)_2$
394		440	460
328	320	315	
256	240	273	230

[a] Wavelengths in nm.

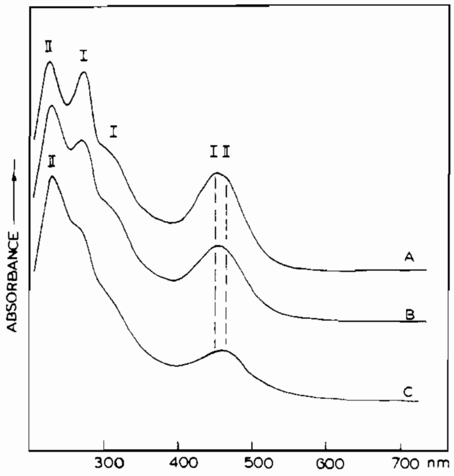

Figure 5. Matrix ultraviolet–visible spectra observed on cocondensing Cu atoms with $^{12}C_2H_2$ at (A) 10–12 K followed by warm-ups to (B) 50 K and (C) 70 K.

spectrum depicts the presence of a single species absorbing strongly at 245 nm, with an indication of a weak shoulder around 320 nm. In conjunction with the comparable infrared behavior for the two complexes designated I and II, the 394-, 328-, and 256-nm absorptions were associated with species I, $Ni(C_2H_2)$, and the 320- and 245-nm absorptions with species II, $Ni(C_2H_2)_2$. Codeposition of nickel atoms with pure acetylene at 60 K resulted primarily in the formation of species II, $Ni(C_2H_2)_2$, as indicated by the intense band at 245 nm, with just a trace of the low-energy bands ascribed to species I, $Ni(C_2H_2)$. One again, this behavior was consistent with that of the corresponding infrared experiments. Ligand concentration experiments in the range C_2H_2/Ar = 1/10–1/100 revealed no absorptions, other than those of uncomplexed Ni atoms[40] and species I and II. The optical spectra are summarized in Table IV.

Copper Atom–Acetylene Reactions. Experiments similar to those performed for Ni atoms were repeated with copper atoms. On codeposition with pure acetylene at 10–12 K, a visible band was observed at 440 nm with accompanying ultraviolet bands at 315 and 273 nm. Annealing experiments, to 50 K (Figure 5), demonstrated that the 315- and 273-nm bands decreased in intensity, in unison with the 440-nm band. Further warming to 70 K resulted in a small, but reproducible, red shift of the visible band to 460 nm (cf. $Cu(C_2H_4)$, 420 nm → $Cu(C_2H_4)_2$, 480 nm → $Cu(C_2H_4)_3$, 486 nm[17]), an increase in the intensity of a band at 230 nm, and the disappearance of the two absorptions at 315 and 273 nm. Comparison with the nickel data confirmed the presence of two distinct molecular species, in accord with the infrared data. From these results it was apparent that the 440-, 315-, and 273-nm excitations could be associated with $Cu(C_2H_2)$ and the 460- and 230-nm absorptions with $Cu(C_2H_2)_2$. The optical data are summarized in Table IV.

Table V. Geometry Used for the Xα Calculations of $M(C_2H_2)$ (Where M = Ni, Cu)

atom	x[a]	y[a]	z[a]
outer sphere	0.00	0.00	0.00
Cu or Ni	0.00	0.00	0.00
C	0.00	1.1433	−3.6284
	0.00	−1.1433	−3.6284
H	0.00	3.1465	−3.6284
	0.00	−3.1465	−3.6284
empty sphere 1	0.00	0.00	4.1100
empty sphere 2	0.00	2.7705	3.0294
	0.00	−2.7705	3.0294

[a] All positions reported in multiples of the Bohr radius of the hydrogen atom.

Table VI. α Values and Radii Used in the Xα Calculations of $M(C_2H_2)$ (M = Ni, Cu)

atom	α value	radius[a]
	$Ni(C_2H_2)$	
outer sphere	0.73592	5.9200
Ni	0.70896	2.2863
C	0.75928	1.5179
H	0.77725	1.1216
empty sphere 1	0.73592	1.8237
empty sphere 2	0.73592	1.8237
	$Cu(C_2H_2)$	
outer sphere	0.73359	5.9494
Cu	0.70697	2.2490
C	0.75928	1.5553
H	0.77725	1.1468
empty sphere 1	0.73359	1.8610
empty sphere 2	0.73359	1.8563

[a] Radii reported in multiples of the Bohr radius of the hydrogen atom.

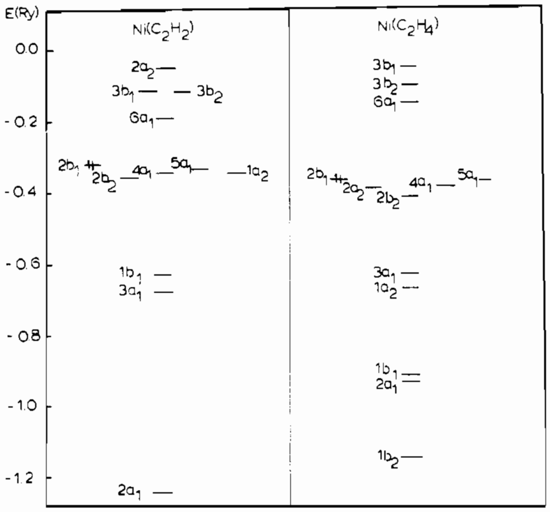

Figure 6. SCF–Xα–SW spin-restricted, ground-state molecular orbital energy level schemes for $Ni(C_2H_2)$ and $Ni(C_2H_4)$.

SCF–Xα–SW Calculations for $Cu(C_2H_2)$ and $Ni(C_2H_2)$. With use of the SCF–Xα–SW technique, molecular orbital energy level schemes and excitation energies were calculated for $Ni(C_2H_2)$ and $Cu(C_2H_2)$, with the acetylene ligand bonded to the respective metal in a side-on C_{2v} configuration. Geometry optimizations were not undertaken in this study for either complex, nor were the bond angles or bond distances changed on passing from $Ni(C_2H_2)$ to $Cu(C_2H_2)$ (Table V). The acetylene ligand was assumed to be linear, with $r(C\equiv C)$ = 1.21 Å and $r(C—H)$ = 1.06 Å. These distances were taken from the geometry optimization of $Ni(C_2H_2)$ performed by Upton and Goddard,[16a] using a different calculational technique (GVB–CI), and differed from those in free acetylene only in a slight elongation of the $C\equiv C$ bond. The metal–acetylene distance was set at 1.92 Å, which is typical of such metal–ligand combinations. Interstitial or "empty" spheres were also used in constructing the muffin-tin potential, and partial wave expansions were included for values of *L* up to 4 for the outer sphere ("OUT"), 2 for the metal atoms, 1 for the carbon atoms, and 0 for the hydrogen atoms and the empty spheres ("ES1" and "ES2"). Complete structural parameters, α values, and sphere radii are listed in Tables V and VI.

The resulting ground-state molecular orbital energy level schemes are depicted in Figures 6 and 7, with the corresponding pictures for the ethylene complexes included for the purpose of comparison. The values for $Ni(C_2H_4)$ and $Cu(C_2H_4)$ have been taken from previous

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(40) W. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, **15**, 292 (1976).

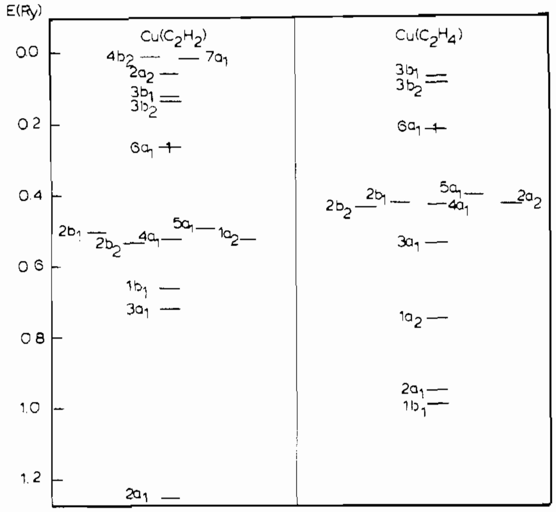

Figure 7. SCF–Xα–SW spin-restricted, ground-state molecular orbital energy level schemes for $Cu(C_2H_2)$ and $Cu(C_2H_4)$.

work.[5,33] The $M(C_2H_2)$ energy schemes (Figures 6 and 7) and the wave function contour diagrams (Figures 8 and 9) portray an interactive picture close to that which would be intuitively predicted on the basis of a Dewar–Chatt–Duncanson model of metal–acetylene bonding,[41] that is, strong acetylene to metal σ donation ($3a_1$) but with varying degrees of metal to ligand back-bonding ($2b_2$). Let us now briefly describe each of the molecular orbital levels in terms of their partial wave analyses (Tables VII and VIII) and in order of increasing energy (Figures 6 and 7).

Apart from the very stable atomic-like core levels of the metal and the carbon atoms, the lowest energy molecular orbitals were those constituting the C–H and C–C σ- and π-acetylene framework ($1a_1$, $2a_1$, $1b_2$). Above these levels can be found the molecular orbital which best characterizes the main acetylene to metal σ-bonding interaction ($3a_1$). It can be described as being composed of a mixture of the C–C in-plane π-bonding orbital and the metal 4s, 4p, and 3d orbitals (Figures 8 and 9 and Tables VII and VIII). The partial wave analysis for the $3a_1$ level of the $Cu(C_2H_2)$ calculations shows both greater metal character and metal d mixing than for the same orbital of the $Ni(C_2H_2)$ analogue (Tables VII and VIII).

The next higher orbital, $1b_1$, can be crudely described as the out-of-plane C–C π bond, with some slight admixture with the metal d_{xz} orbital, indicating a certain amount of out-of-plane π back-donation of charge density. At higher energies occur a group of five closely spaced levels which can be described as primarily metal-localized d orbitals. These include the orbital which, in the Dewar–Chatt–Duncanson scheme, would be considered the in-plane π back-bond ($2b_2$), illustrated in Figures 8 and 9. In line with the higher effective nuclear charge of copper, relative to nickel, one finds that the d manifold is stabilized in $Cu(C_2H_2)$, with respect to $Ni(C_2H_2)$. The highest occupied molecular orbital of $Ni(C_2H_2)$, the d_{xz} orbital ($2b_1$), occurs in this closely spaced d manifold. The highest occupied molecular orbital for $Cu(C_2H_2)$, on the other hand, is the $6a_1$ which is singly occupied and thus gives rise to a $^2A_1$ electronic ground state. This level is primarily composed of the copper 4s orbital with lesser contributions of the carbon 2p orbitals (Figure 8) and is antibonding between the Cu and C_2H_2 moieties. Excitation of the unpaired electron from this level to a higher lying orbital gives rise to the visible absorption in the electronic spectrum of $Cu(C_2H_2)$ and, hence, the color of this species (analogous to the case of $Cu(C_2H_4)$[33]). This Xα ground-state molecular orbital description of $Cu(C_2H_2)$ is in agreement with the ESR proposal of Kasai, based on the observation of large $^{63}Cu/^{65}Cu$ hyperfine coupling constants for $Cu(C_2H_2)$.[23] The $6a_1$ orbital for $Ni(C_2H_2)$ turns out to be the lowest unoccupied molecular orbital (Figure 9) with slightly greater d-orbital character than in $Cu(C_2H_2)$. Because the antibonding $6a_1$ orbital is singly occupied in the case of Cu but unoccupied in the case of Ni, along with the fact that the $2b_2$ orbital for the Cu complex is essentially a metal-localized d orbital (in contrast to the Ni case where there is more C_2H_2 character, justifying the notion of some π-like back-bonding), one would expect that the metal–acetylene bond in $Cu(C_2H_2)$ would be considerably weaker than in $Ni(C_2H_2)$.

The more important orbitals showing the major bonding interactions in the complexes as well as the lowest unoccupied molecular orbitals of $Cu(C_2H_2)$ and $Ni(C_2H_2)$ and the highest occupied molecular orbital of $Cu(C_2H_2)$ are pictured in the wave function contour plots of Figures 8 and 9. Detailed partial wave analyses of all the molecular levels for both $Ni(C_2H_2)$ and $Cu(C_2H_2)$ are to be found in Tables VII and VIII.

The interrelationship between the acetylene calculations of this study and the recently completed ethylene analogues[33] turns out to be quite informative in terms of, for example, understanding common features of their bonding schemes as well as interpretive issues concerning optical trends and electronic assignments (see later). In particular, it may be noted here that the highest occupied molecular orbitals of $Cu(C_2H_2)$ and $Cu(C_2H_4)$ are both of the $6a_1$ type and are both composed primarily of the Cu 4s orbital, similar to that of Cu(CO) ($5\sigma^+$), as demonstrated by optical and ESR spectroscopic and SCF–Xα–SW techniques.[42]

Discussion

A number of points concerning the acetylene complexes of nickel and copper are worthy of detailed discussion, especially those which relate to the corresponding ethylene species. These include a rationalization of the observed spectroscopic trends, a description of the metal–ligand bonding, and an attempt to understand the apparent instability of a tris(acetylene) complex for either metal. This latter point is perplexing in view of the ready synthesis of a wide range of $M(olefin)_3$ species.[43] In addition, the usefulness of these binary π-acetylene complexes as starting models for evaluating the interaction of alkynes with metal surfaces will be pursued in a manner similar to that previously described for metal–olefin chemisorption models.[15,16b,17,34]

The most obvious difference between the nickel/copper–acetylene and the nickel/copper–ethylene systems is the absence of binary complexes of the type $M(C_2H_2)_3$. However, it is not an unprecedented occurrence to isolate a binary bis(acetylene) metal complex of a group 8 metal. Muetterties,[44] for instance, has suggested the formation of $Ni[(CH_3)_3CC{\equiv}CC(CH_3)_3]_2$ as a product of the reaction of $Ni(COD)_2$ with the acetylene ligand while Stone and co-workers[45] have synthesized the complex $[(H_5C_6)C{\equiv}C(C_6H_5)]_2Pt$. It may be argued that the pseudotetrahedral geometry of the latter complex, with a 27° bend-back angle for the bulky phenyl groups, is the result of a steric effect.[46] However, in the $M(C_2H_2)_2$ complexes of the present study one cannot consider hydrogen as a bulky substituent. It may be noted, though, that for a hypothetical $Ni(\pi\text{-}C_2H_2)_3$ complex, with an H—C—C bend-back angle of 5° (based on Upton and Goddard's optimized structure for $Ni(\pi\text{-}C_2H_2)$[16a]), an "all-planar" idealized D_{3h} geometry can be shown to exhibit considerable steric interaction between the hydrogen atoms of the coordinated acetylene ligands, in contrast with the "all-planar" $Ni(C_2H_4)_3$ complex (see Figure 10). (This geometry has been predicted as the most stable conformation by EHMO and ab initio calculations for $Ni(C_2H_4)_3$ by Hoffmann and Rösch[12] and Pitzer and Schaefer[14] and is supported by crystal structures such as those for $Pt(C_2F_4)(C_2H_4)_2$ and $Pt(C_7H_{10})_3$.[47])

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(46) J. Fornies, M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1006 (1977).

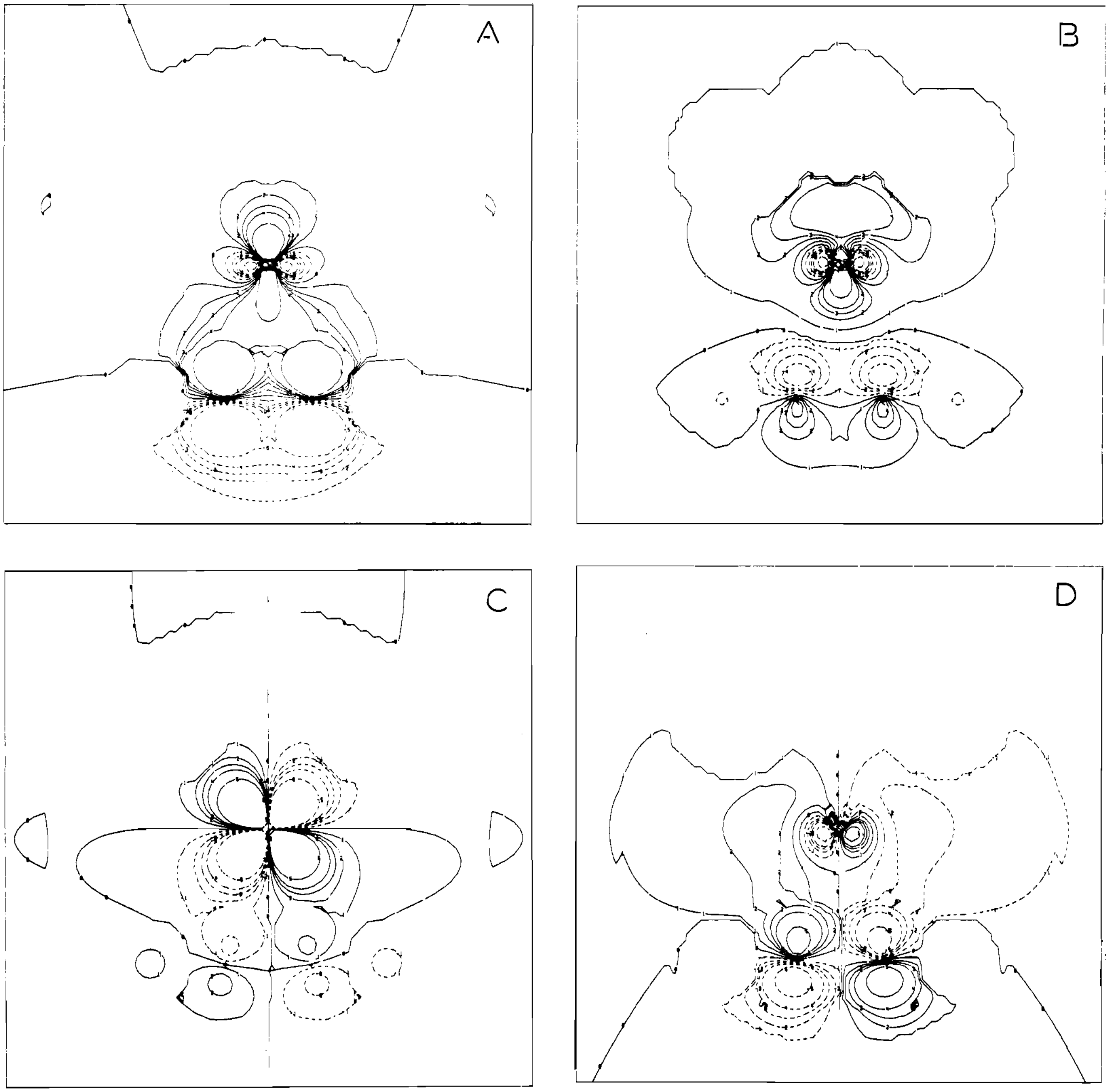

Figure 8. Wave function contour diagrams for selected molecular orbitals of $Cu(C_2H_2)$: (A) $3a_1$, (B) $6a_1$, (C) $2b_2$, and (D) $3b_2$. Note that positive wave function contours are indicated by a solid line, while negative wave function contours are given by dashed lines. Contour specifications: 1 = 0.03, 2 = 0.06, 3 = 0.08, 4 = 0.10, 5 = 0.15 in units of $(\text{electrons}/(\text{bohr radius})^3)^{1/2}$. The "0" contours represent nodal surfaces.

It is interesting to speculate on the (chemical) implications of the coordination of an additional acetylene ligand to $Ni(C_2H_2)_2$. It is possible that a larger bend-back angle on the ligands would be induced to help minimize this steric interaction. This could make the tris(acetylene) complex susceptible to further reaction such as in an insertion–oligomerization process. Support for this proposal stems from two sources. Although the absorbances of the binary nickel–acetylene complexes decayed to zero at roughly 175 K in these studies, at room temperature there remained on the optical window an, as yet, unidentified, yellow, air-stable residue. The product could be an organometallic species since normally the residue of a nickel atom matrix experiment is a black metallic film. Moreover, Lagowski concluded that a Ni(II) metallocycle could well be a reaction intermediate from an analysis of the oligomerization products formed in his studies on the reactions of alkynes with transition-metal atoms.[26] Rehybridization of this type is common in organometallic cluster chemistry, and acetylene and monosubstituted acetylenes are easily trimerized.[48] This does not preclude the possibility of cluster complex involvement, particularly in view of the elevated temperatures of these matrix experiments and the, previously mentioned, possibility of the occurrence of heterogeneous metal atom cryogenic reactions.[43]

The optical spectra of $Cu(C_2H_2)$ and $Ni(C_2H_2)$ show both similarities and differences when compared with those of

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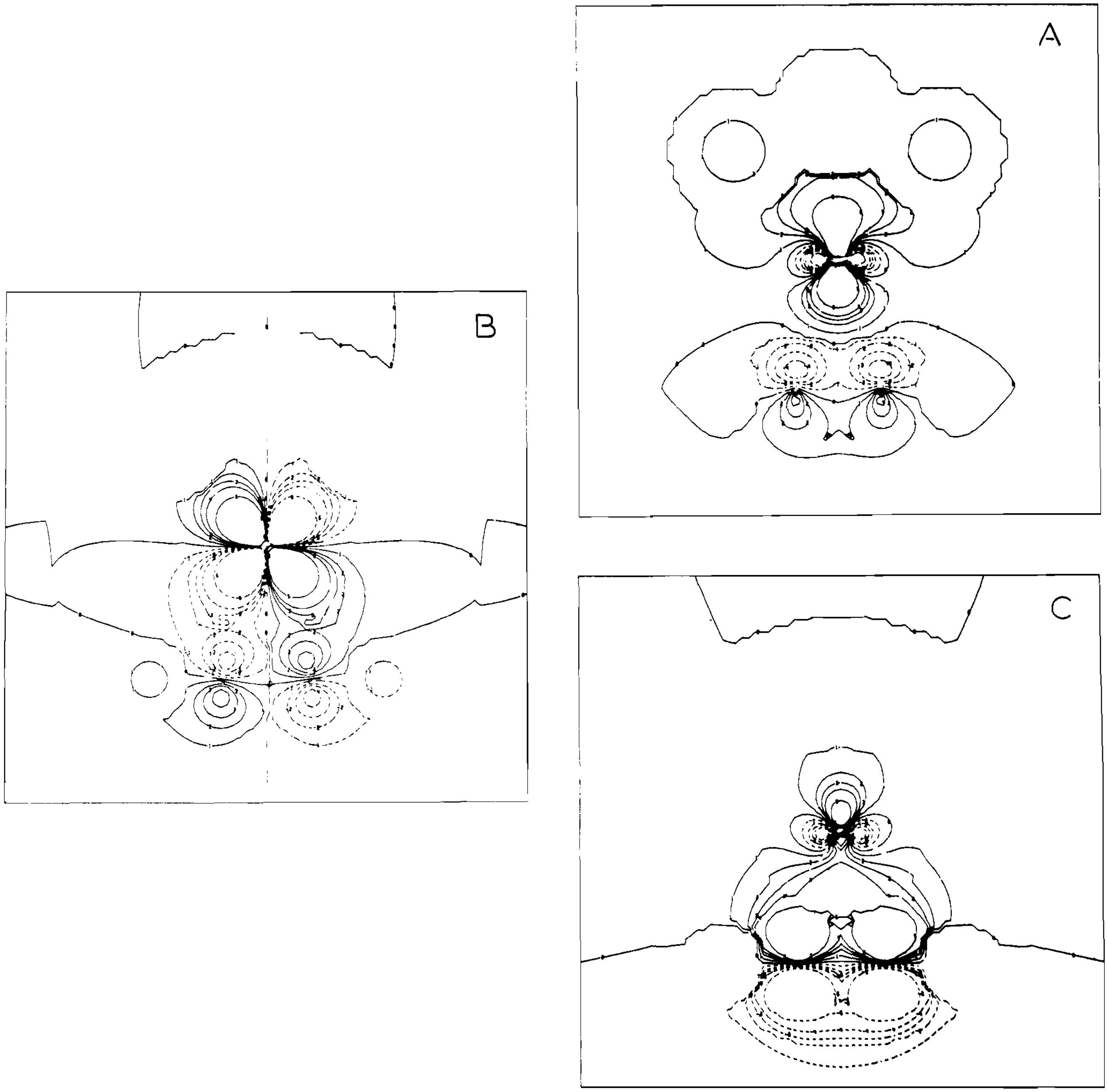

Figure 9. The same as Figure 8 but for selected wave functions of $Ni(C_2H_2)$: (A) $6a_1$, (B) $2b_2$, and (C) $3a_1$. See Figure 8 for orbital and contour specifications.

$Cu(C_2H_4)$ and $Ni(C_2H_4)$. It may be recalled that for $Cu(C_2H_2)$ three absorptions were observed while for $Cu(C_2H_4)$[17] only two absorptions were clearly identified. In both cases, one absorption was centered in the visible region of the optical spectrum. For $Ni(C_2H_2)$ three absorptions were also observed, the lowest energy band being in the near ultraviolet around 394 nm, in contrast to $Ni(C_2H_4)$[16b,36,43] for which only a single ultraviolet absorption was observed (320 nm).

Because of the low symmetry of the molecule, there are many possible excitations to take into account. Referring initially to the energy level scheme of $Ni(C_2H_2)$ (Figure 6), one may make a number of plausible assignments. It may be argued that the lowest energy band of $Ni(C_2H_2)$ should be of the HOMO to LUMO variety. Thus, one might assign the 394-nm absorption to an electronic excitation involving the $2b_1$ and $6a_1$ levels. However, since these two orbitals have out-of-plane and in-plane orientations, respectively, it might be expected that the intensity of such a transition would be low. From this point of view it might be argued that any of the $5a_1$ to $6a_1$, $4a_1$ to $6a_1$, or $2b_2$ to $6a_1$ excitations would be a better choice. Likewise, the 328-nm absorption could be assigned to any of the $2b_1$ to $3b_1$, $5a_1$ to $3b_2$, $4a_1$ to $3b_2$, or $2b_2$ to $3b_2$ excitations, taking into account both symmetry and intensity considerations. The highest energy band of $Ni(C_2H_2)$, centered at 256 nm, is also the most intense. The most likely assignment for this transition is the one involving the excitation of an electron from the $1a_2$ level to the $2a_2$ orbital. This would correspond to the promotion of an electron from the metal d_{xy} orbital to the nonbonding π^* orbital of the C_2H_2 ligand. As such, it would represent a metal to ligand charge-transfer type of transition and would be expected to be very intense, as is the case. These energy values and optical assignments are collected in Table IX. Because of the very large number of possible excitations, transition-state calculations were not performed. Typically one would expect an increase on the order of 5–15% over the values obtained on

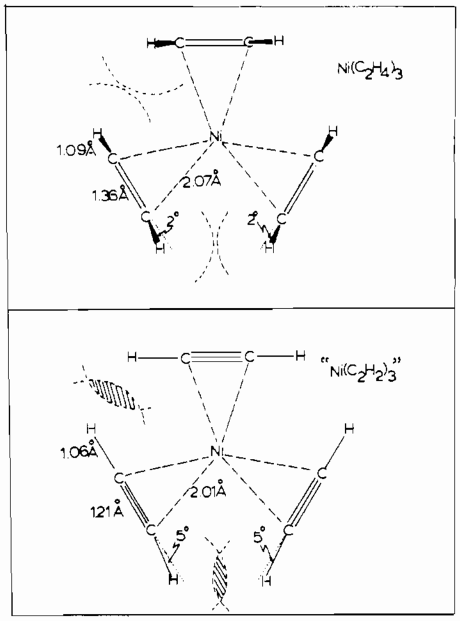

Figure 10. Scale drawings of known D_{3h} planar Ni(π-C_2H_4)$_3$ and hypothetical D_{3h} planar Ni(π-C_2H_2)$_3$ complexes. The van der Waals radius for H was assumed to be 1 Å; structures were based on the GVB–CI geometry optimized calculations of Upton and Goddard.[16a] Note that the C–H bonds in Ni(π-C_2H_4)$_3$ are represented by a projection into the molecular plane.

Table IX. Spectroscopic Assignments for Ni(C_2H_2) and Cu(C_2H_2) Based on SCF–Xα–SW Calculations

obsd		calcd[a]	
nm	cm^{-1}	cm^{-1}	assignt
		Ni(C_2H_2)	
394	25 400	13 200	$2b_1 \rightarrow 6a_1$
		14 300	$5a_1 \rightarrow 6a_1$
		15 100	$4a_1 \rightarrow 6a_1$
		16 900	$2b_2 \rightarrow 6a_1$
328	30 500	23 100	$2b_1 \rightarrow 3b_1$
		24 000	$5a_1 \rightarrow 3b_2$
		24 700	$4a_1 \rightarrow 3b_2$
		26 600	$2b_2 \rightarrow 3b_2$
256	39 100	32 200	$1a_2 \rightarrow 2a_2$
		Cu(C_2H_2)	
440	22 700	13 800	$6a_1 \rightarrow 3b_2$
315	31 700	26 000	$5a_1 \rightarrow 6a_1$
		26 800	$2b_1 \rightarrow 6a_1$
		29 100	$4a_1 \rightarrow 6a_1$
		30 000	$2b_2 \rightarrow 6a_1$
273	36 600	39 800	$5a_1 \rightarrow 3b_2$
		41 500	$2b_1 \rightarrow 3b_1$
		42 900	$4a_1 \rightarrow 3b_2$
		43 800	$2b_2 \rightarrow 3b_2$

[a] Based on differences of the ground-state eigenvalues.

the basis of ground-state eigenvalue differences.[33] While these assignments cannot be considered to have been conclusively proved, they do represent the most plausible set that could be made at the present time. Their confirmation will have to await further studies.

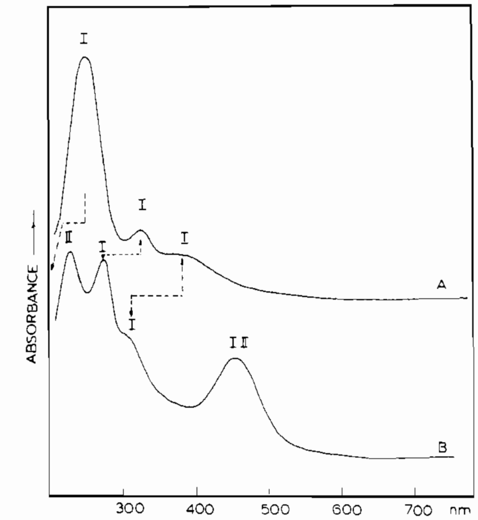

Figure 11. Optical spectra showing the correlation of transitions of a common origin for (A) Ni(C_2H_2) and (B) Cu(C_2H_2), both recorded in solid C_2H_2 matrices.

Table X. Summary of the Optical Data for the Monoethylene and Monoacetylene Complexes of Nickel and Copper[a]

Cu(C_2H_4)[b,c]	Cu(C_2H_2)	Ni(C_2H_2)	Ni(C_2H_4)[c]
420	440		
380	315	394	320
	273	328	
	d	256	

[a] Wavelengths in nm. [b] Data taken from ref 23. [c] Data taken from ref 8b, 40, 41, and 48. [d] Not observed—probably below the energy cut-off of the spectrophotometer.

A comparison of the optical spectra of Ni(C_2H_2) and Cu(C_2H_2) (Figure 11) reveals some interesting electronic properties of the two complexes. Apart from the ultraviolet absorption ascribed to Cu(C_2H_2)$_2$ and the overlapping visible absorptions of the monoacetylene and bis(acetylene) complexes of copper, it may be noted that the ultraviolet absorptions of Cu(C_2H_2) have shifted to higher energies, with respect to those previously discussed for Ni(C_2H_2). This trend is, in fact, so pronounced that the Cu(C_2H_2) counterpart of the 256-nm band of Ni(C_2H_2) lies at an energy beyond the range of the spectrophotometer. With reference to the energy level schemes (Figures 6 and 7) and the optical spectra of the two complexes (Figure 11), it is clear that the visible absorption of the monoacetylene complex of copper can be associated with the excitation of the unpaired electron in the $6a_1$ orbital to a higher energy level, most likely the $3b_2$. This is identical with the situation found for Cu(C_2H_4).[33] With the trend of the ultraviolet bands in mind, assignments can be made for the visible and ultraviolet absorptions of the Cu(C_2H_2) complex. These are presented in Table IX, along with the similar set for Ni(C_2H_2).

It may be noted that the Xα calculations of the present study correctly predicted the shift to higher energies of the ultraviolet absorptions of Cu(C_2H_2), compared with those of Ni(C_2H_2). This can be easily seen either from the energy level schemes for the two complexes (Figures 6 and 7) or from the calculated transition energies collected in Table IX. This effect is largely a manifestation of the increased stability of the copper d orbitals, relative to those of nickel. In effect, the d orbitals of copper are acting more like a closed-shell core level than those of nickel. This is also reflected in the greater percentage metal d character of the molecular orbitals of Cu(C_2H_2) grouped about the −0.51-Ry energy value compared with the similar set for Ni(C_2H_2), which are to be found in the region of −0.33 Ry. Although there is a corresponding drop in the energies of the higher lying molecular orbitals of Cu(C_2H_2) such as the $6a_1$, the $3b_2$, the $3b_1$, and the $2a_2$, the stabilization of the d-like molecular orbitals is much more dramatic, and hence the corresponding transitions involving excitations of electrons from these orbitals to the unoccupied set occur at higher energies than those for Ni(C_2H_2).

It is interesting to note the correspondence between other observed and calculated trends of the copper and nickel monoacetylene and monoethylene complexes. These may be dealt with in turn with the aid of Table X, which contains a summary of the optical data for all four organometallic species. Referring to Figure 7, it may be noted that one would expect, on the basis of differences in the ground-state Xα eigenvalues, to find a slight increase in the transition energy of the visible band on passing from $Cu(C_2H_2)$ to $Cu(C_2H_4)$. This is indeed the case found experimentally (Table X). Likewise, one would predict a decrease in the energy of the major ultraviolet band of $Cu(C_2H_4)$ compared with the similar absorption found for $Cu(C_2H_2)$. (This excitation corresponds to the promotion of an electron from the metal d set to the partially occupied $6a_1$ orbital.) Reference again to Table X bears out this relationship. In the case of the two nickel complexes, it may be easily seen from Figure 6 that not only does one expect to find a greater number of ultraviolet bands in the case of the monoacetylene complex but that the lowest energy band should also lie at a lower energy than the corresponding HOMO to LUMO transition of $Ni(C_2H_4)$. Once again this is borne out by experiment (Table X). (On the basis of the ground-state eigenvalue differences, it is also interesting to note, in passing, that one would predict that the energy of the middle transition of $Cu(C_2H_2)$ should be very nearly equal that of the middle band of $Ni(C_2H_2)$. Again the correspondence between experiment and theory is excellent.) Finally, a comparison may be made between the two ultraviolet bands of the monoethylene complexes of copper and nickel. One would expect to find the energy of the transition for $Ni(C_2H_4)$ to be slightly greater than that for $Cu(C_2H_4)$. This is borne out, as well, by experiment (Table X).

Turning to the subject of metal–acetylene chemisorption models, one finds that direct surface counterparts are apparently lacking. While π-chemisorbed acetylene has been proposed to exist at 140 K on Ni(111) surfaces,[2a] a recent reinterpretation of this UPS data in the light of HREELS measurements and a more refined theoretical analysis[22b] has led to the suggestion that the surface acetylene species has been extensively rehybridized.

A brief survey of the types of surface species that can result from acetylene chemisorption reveals that, depending on conditions of temperature and coverage, metal type, and crystal plane, extensive rehybridization, rearrangements, or fragmentations may occur. For example, C_2H_2 on Ni(111)[18] and Pt(111)[20] at 140 K show HREELS spectra characteristic of a surface species with a substantially reduced bond order. On the nickel surface, it was estimated to be close to 1.15 with the acetylene being adsorbed on a threefold site through two σ bonds and one π bond. Adsorption on Pt ($180 \leq T \leq 300$ K) resulted in an acetylene surface species with a bond order of 1.75, based on the observation of a vibration around 1200 cm^{-1} (ascribed to a ν(C=C) stretching mode).

At higher temperatures more dramatic structural alterations can occur, either from reorganization of the acetylene backbone or by reaction with background hydrogen. This can lead to surface vinylidene and ethylidene species.[19,20] Even more extensive structural rearrangements have been observed, leading to either preferential CC triple bond fission to yield CH species[21] or CH fission to yield C_2, C, and H species.[22b]

Thus, it is clear that acetylene–surface interactions involve more than simple π coordination of the ligand to an active site. The initial interaction of acetylene with a metal surface could be viewed as occurring through a π-type intermediate. Once adsorbed, though, it is clear that extensive structural rearrangements occur.

Table XI. Variational Spectra of $Ni(C_2H_2)$ and C_2H_2 Chemisorbed on Ni(111)[a]

$Ni(C_2H_2)$ IR (matrix)	$Ni(C_2H_{2,ads})$[b] HREELS (surface)	C_2H_2[c] IR (gas)	tentative assignt
		3287	ν(C–H)
3130			ν(C–H)
	2910		ν(C–H)
1734			ν(C≡C)
	1230		ν(C=C)
	870		δ(H–C–H)
		729	δ(H–C–H)
572			ν(Ni–C)
	510		ν(Ni–C)

[a] Frequencies in cm^{-1}. [b] Data taken from ref 49. [c] Data taken from G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. II, Van Nostrand, Princeton, M.J., 1945.

A comparison of the vibrational data for $Ni(C_2H_2)$ with that of the chemisorbed form of acetylene on nickel serves to emphasize the extent of rehybridization of the organic ligand on the metal surface (see Table XI). Clearly, there is little correspondence between the matrix data and the HREELS surface data. There is a difference of some 200 cm^{-1} in the ν(C—H) modes. Moreover, the surface complex shows no ν(C≡C) in the 1800–1700-cm^{-1} region, characteristic of π-bonded acetylene species. In the mononuclear complexes $Cu(C_2H_2)$ and $Ni(C_2H_2)$, the acetylene ligand displays a shift in the frequency of the ν(C≡C) mode of roughly 100 and 200 cm^{-1}, respectively, upon coordination. In the surface complex, a ν(C=C) mode, assigned on the basis of frequency invariance to C_2D_2 substitution, occurred at 1230 cm^{-1}. This frequency does not correspond to any of the vibrational absorptions in the two molecular complexes (although one cannot preclude band overlap with an intense C_2H_2 absorption around 1300 cm^{-1}). It is also clearly too low in energy to be assigned to a coordinated triple bond. This strongly reinforces the formulation of the surface complex as a di-σ rehybridized species, with a significantly lowered C—C bond order. The lower frequency of the ν(C—H) stretching mode could be the result of such a rehybridization, although such an assignment is not entirely self-evident.[36] Alternatively, the difference in this frequency might indicate a surface–hydrogen interaction analogous to that displayed in the C_2H_4/Ni(111) chemisorption system,[49] which showed a "softened" ν(C—H) stretching mode at 2690 cm^{-1}. It would appear, then, that the organometallic species of the present study cannot be directly compared with known acetylene–surface intermediates. However, it is quite possible that they would be appropriate models for precursor or short-lived π-acetylene species, probably observable at low temperatures.

Conclusions

Two mononuclear acetylene complexes have been synthesized and characterized for both nickel and copper, the former being considerably more thermally stable than the latter. In both cases, the vibrational and electronic properties of these molecules can be understood in terms of a π-bonded acetylene ligand. With respect to providing test cases for a localized bonding view of acetylene chemisorbed in a π-type fashion on nickel or copper surfaces, however, no clear analogies could be made because of the lack of vibrational data for a surface species that could be identified as a π-bonded entity. Because of this, it would be unreasonable to expect there to be much of a correspondence between the vibrational data of the present study and that of surface–acetylene investigations. In this regard, the results of this matrix isolation study would tend to reinforce the view of recent surface investigations that

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acetylene is extensively rehybridized when chemisorbed onto group 8 metal surfaces.

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Registry No. $^{12}C_2H_2$, 74-86-2; $^{13}C_2H_2$, 35121-31-4; $Ni(^{12}C_2H_2)$, 65583-93-9; $Ni(^{13}C_2H_2)$, 76900-64-6; $Ni(^{12}C_2H_2)_2$, 76900-65-7; $Ni(^{13}C_2H_2)_2$, 76900-66-8; $Cu(^{12}C_2H_2)$, 65881-80-3; $Cu(^{13}C_2H_2)$, 76900-67-9; $Cu(^{12}C_2H_2)_2$, 65881-79-0; $Cu(^{13}C_2H_2)_2$, 76900-68-0; $Cu(^{12}C_2H_2)(^{13}C_2H_2)$, 76900-69-1.

Supplementary Material Available: Tables VII and VIII, energies, % charges, and partial wave analyses for $Ni(C_2H_2)$ and $Cu(C_2H_2)$, respectively (10 pages). Ordering information is given on any current masthead page.

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Molecular Orbital Calculations for the Reaction Fragment NSN

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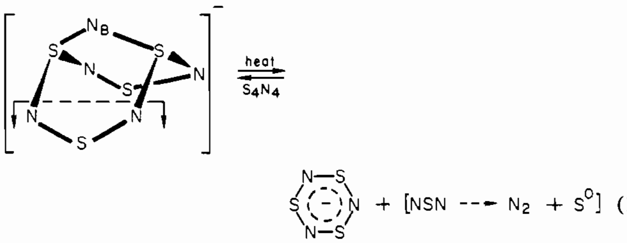
An ab initio Hartree–Fock–Slater procedure is employed to reveal local energy minima for two symmetric NSN species NSN90 and NSN180. An additional NSN species leading to a decomposition channel of $N_2 + S$ is also characterized. The linear NNS species is examined for comparison to the symmetric species. These results are discussed in the context of recent experiments on sulfur–nitrogen species.

Introduction

A number of reactions have recently been discovered[1] which involve the transfer of an NSN fragment to or from a sulfur–nitrogen system as, for example, in the reaction shown in eq 1. This reaction suggests the possibility that the NSN moiety might be transferred, as such, with a finite mean lifetime. However, attempts to detect this species have not been successful to date.



(1)

The only dinitrogen–sulfur species for which there is even tentative claim to experimental characterization[3b] is the N_2S species for which a linear NNS structure appears to be most favorable.[3a] Nevertheless, since the reaction scheme given in eq 1 involves the cleavage of a symmetrical (linear or bent) NSN structure, one might still wonder whether a metastable NSN species could be involved. Further since the reaction products in these systems are found to be N_2 and elemental sulfur[2] or the oligimer S_8[1], there is the question of the decompostion channels of any such metastable species.

To explore these possibilities we have employed an ab initio Hartree–Fock–Slater procedure with which we have previously successfully treated nitrogen–sulfur systems.[4] The method utilizes a double-ζ basis augmented with sulfur d orbitals and invokes a "frozen" core in the manner described by Baerends and Ros.[5] The calculations were of the single determinant spin restricted type, and all species considered were singlets. The total statistical energy was used as a probe of molecular conformation stability.[5] The energy surface for the arrangement NSN can be taken to depend on the three variables θ_{NSN}, the angle at S subtended by the nitrogens N_1 and N_2, and the two "bond" lengths R_{SN_1} and R_{SN_2}. In the case of the *symmetric* distortions, which we wish to consider, $R_{SN_1} \equiv R_{SN_2}$, and the problem of finding the energy minimum is reduced to a search in the two variables θ_{NSN} and R_{SN}.

For purposes of comparison we carried out our minimization procedure to obtain the most favorable bond lengths for the linear asymmetric species NNS.

Results

A local minimum in the total statistical energy surface was obtained for $\theta_{NSN} = 180°$ and $R_{SN} = 1.47$ Å for the valence electronic configuration $\sigma_g{}^4\sigma_\mu{}^4\pi_g{}^4\pi_\mu{}^4(D_{\infty h})$. We denote this configuration by NSN180, and in Figure 1 we sketch the energy as a function of θ_{NSN} for the optimum distance $R_{SN} = 1.47$ Å. For subsequent reference we give the dependence of this same electronic configuration as a function of θ_{NSN} but for $R_{SN} = 1.63$ Å.

Some 65 kcal above the energy of the NSN180 species we could locate another local minimum near $\theta_{NSN} = 90°$ and $R_{SN} = 1.63$ Å with a valence electronic description given by $a_1{}^8a_2{}^2b_1{}^2b_2{}^4$ (C_{2v}). Denoting this case by NSN90 we sketch, in Figure 1, its dependence on θ_{NSN} for the optimum distance $R_{SN} = 1.63$ Å. For subsequent reference we sketch the energy

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