Communication

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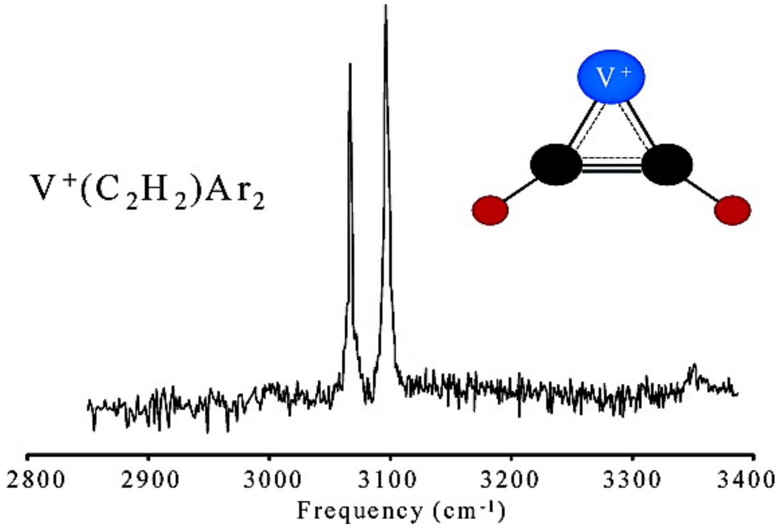

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Structural Trends in Transition Metal Cation−Acetylene Complexes Revealed through the C−H Stretching Fundamentals

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Although transition metal−acetylene complexes are prototypes for π-bonding in organometallic chemistry,[1−3] the vibrational spectroscopy of these systems has been limited to studies in condensed phases. However, gas-phase ion complexes can be studied in isolation, revealing individual molecular properties.[2−4] Mass spectrometry provides bond energies and reactivities of metal ion−acetylene complexes.[2,3,5] Electronic spectroscopy has probed excited states.[6,7] Geometries and electronic structures have been investigated theoretically.[8−10] IR spectroscopy is a key tool in organometallic chemistry,[11] but the low concentration of gas-phase ions precludes conventional absorption spectroscopy. However, resonance-enhanced photodissociation (IR-REPD) spectroscopy using new IR lasers now allows vibrational spectra of ions to be measured in the gas phase.[12−14] This method found cyclization reactions of acetylene in larger $Ni^+(C_2H_2)_n$ clusters.[12] We now report the IR spectra of mono-ligand $M^+(C_2H_2)$ complexes (M = V, Fe, Co, Ni), which reveal new trends in metal−ligand interactions.

$M^+(C_2H_2)$ complexes produced by laser vaporization (355 nm) were studied in a molecular beam environment. Ions were mass-selected in a reflectron time-of-flight spectrometer and excited with a tunable IR-optical parametric oscillator (OPO) laser.[13] The argon tagging method was employed.[13] Photoelimination of argon occurs on resonance, mapping the IR absorptions for these complexes; the yields mirror the IR intensities. The OPO tuning range only allows investigation of the C−H stretching region. The results were interpreted in conjunction with density functional theory (DFT) computations[15] at the B3LYP[16]/6-311+G** and B3LYP/6-311+G-(3df,2p) levels.

Experimental data are limited,[5] but theory finds $M^+(C_2H_2)$ dissociation energies to be 30−45 kcal/mol (10 500−15 700 cm^{-1}).[8−10] Excitation in the C−H stretching region therefore cannot produce photodissociation except by multiphoton absorption, which is inefficient. As expected, virtually no fragmentation is observed for the bare $M^+(C_2H_2)$ complexes. Argon tagging provides a low energy fragmentation channel with minimum perturbation of the metal−ligand interaction.[13] Consequently, tagged species closely approximate the spectra of isolated complexes. M^+Ar binding energies are 1000−4000 cm^{-1},[17−19] and the per-atom binding energy is generally less in multi-argon complexes. Weak signals are found for mono-argon complexes because dissociation is still inefficient for these systems. Fragmentation is greatly enhanced when two argons are present. Figure 1 shows the IR-REPD spectra of $M^+(C_2H_2)Ar_2$ (M = V, Fe, Co, Ni) species in the 2900−3400 cm^{-1} region, measured in the mass channel for the loss of one argon.

The IR spectrum for each complex has two bands due to the asymmetric and symmetric C−H stretches of the acetylene ligand. While the symmetric stretch is not IR-active in free acetylene, symmetry breaking activates this mode in the metal complexes. The Ni^+ spectrum shows satellite bands because the $^2A_1$ and $^2B_1$ states are nearly isoenergetic[9] (as we confirm here) and both are populated. The frequencies of these two states are almost the same.

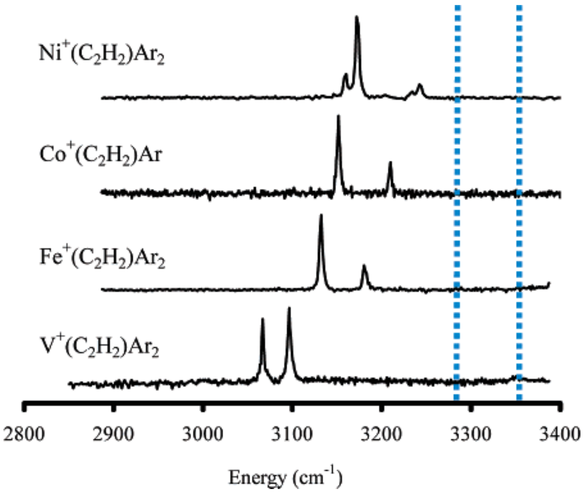

Figure 1. IR-REPD spectra for $M^+(C_2H_2)Ar_2$ complexes. The acetylene frequencies[20] at 3289 and 3374 cm^{-1} are shown in blue.

All of the bands in these cation complexes are shifted to the red from the C−H stretches in acetylene, in accord with the Dewar−Chatt−Duncanson (DCD) complexation model.[10,11] As seen for metal carbonyls, acetylene π-electrons are donated into empty metal *d* orbitals, while filled metal *d* orbital electrons back-donate into acetylene π*-antibonding orbitals. Both of these weaken the CC bonding and increase the *p* character of the carbon hybridization. This was shown by previous condensed phase studies[11] of the C≡C stretch (near 1974 cm^{-1}, outside our IR tuning range). The same effect reduces the C−H stretching frequencies.

The magnitude of the shifts of the C−H vibrations for different metals is intriguing. The shift is greatest for $V^+(C_2H_2)$ and is progressively smaller for the Fe^+, Co^+, and Ni^+ complexes. This pattern is surprising, because it does not track the available theoretical and experimental metal cation−acetylene complexation energies,[5,8−10] as discussed below. For Fe^+, Co^+, and Ni^+, the symmetric stretch is much less intense (Figure 1) because it only becomes IR-active via distortion of the HCC angle. For $V^+(C_2H_2)$, however, the symmetric stretch band is more intense.

Theory reproduces and explains these features. The computed ground-state C−H stretching vibrations for each $M^+(C_2H_2)$ and its Ar-tagged complexes are quite close to the experimental values (Table 1). The IR oscillator strengths match the experimental intensities (Figure 1). Our results are consistent with earlier computations on various states of these complexes.[8,9] The argons induce only small band shifts (16 cm^{-1} or less) vs the free ion. The larger differences in going from one metal to another separate $V^+(C_2H_2)$ ($^3A_2$) from the $^nB_1$ group. The variation from Fe^+ to Co^+ to Ni^+ is nearly constant (ca. 21 and 32 cm^{-1} for the experimental asymmetric and symmetric stretch, respectively).

As noted before,[8] the $M^+(C_2H_2)$ complexes of the late transition metals are bound primarily by electrostatic forces, the $M^+-C_2H_2$

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Table 1. Computed and Experimental (±1 cm^{-1}) Vibrational Frequencies[a]

	theory[b]		experiment	
M^+(state)	$M^+(C_2H_2)$	$M^+(C_2H_2)Ar$	$M^+(C_2H_2)Ar_2$	$M^+(C_2H_2)Ar_2$
$V^+(^3A_2)$	3060(49)	3062(39)	3063(32)	3067
[1.724]	3093(44)	3099(41)	3095(37)	3097
$Fe^+(^4B_1)$	3125(145)	3130(130)	3129(110)	3132
[1.086]	3193(44)	3198(52)	3193(42)	3181
$Co^+(^3B_1)$	3132(185)	3139(164)	3147(154)	3152
[1.010]	3206(36)	3213(44)	3222(43	3210
$Ni^+(^2B_1)^c$	3156(232)	3162(214)	3171(195)	3160
[0.967	3240(27)	3247(34)	3255(35)	3233
$Ni^+(^2A_1)^c$	3178(195)	3172(209)	3178(195)	3174
[0.996]	3263(23)	3259(33)	3264(34)	3244

[a] Theoretical intensities are in parentheses, and metal charges are in brackets. [b] Frequencies are at B3LYP/6-311+G**, scaled by 0.960. $M^+(C_2H_2)$ results at B3LYP/6-311+G(3df,2p), scaled by 0.964, are nearly identical. Natural charges are given at the latter level. [c] The $^2B_1$ and $^2A_1$ states lie at nearly the same energy; $^2A_1$ is assigned as the ground state to match the higher measured frequencies of the more intense bands.

separations are moderately large, and the distortion of the acetylene is modest. Consistent with this, the red shifts from acetylene are smaller for the Fe^+, Co^+, and Ni^+ complexes. The HCC angles,[8] 150−166° in our computations of the $^nB_1$ states, bend sufficiently to activate the symmetric CH stretch, but these are weak in intensity. The Fe^+, Co^+, and Ni^+ complexes favor the higher multiplicity $^nB_1$ state with only small DCD involvement of the metal *d* and acetylene orbitals. The metal charges are near unity, but decrease regularly from Fe (1.086) to Co (1.010) to Ni (0.967/0.996).

In sharp contrast, early transition metals (V, Ti, Sc) form covalent metallacycles with shorter M^+-C and longer CC bonds, as well as smaller HCC angles. Lower multiplicity states are preferred.[9] (Our $^3A_2-^5B_1$ energy difference for V^+ is 5 kcal/mol and is larger for Ti and Sc.) These $^nA_2$ states have a doubly occupied b_2 MO with considerable metal *d* involvement, which confers M−C bonding and C−C antibonding character. In the b_2 MO, the filled metal *d* orbital donates electron density into the in-plane antibonding π^* MO of acetylene. Because of this "back-bonding," the natural charge of vanadium is much larger in the $^3A_2$ (+1.724) than that in the $V^+(C_2H_2)$ $^5B_1$ (+1.051) state. In addition, donation from acetylene also is evident, particularly in the filled b_1 MO, which has aromatic 2π-electron cyclopropenium character. The reduction of the C−C bond order and the change in the carbon hybridization[9] decreases the HCC angle to 142.3° in the $^3A_2$ state (vs 165.7° in its $^5B_1$ state). Like cyclopropene and cyclopropenylidene (also computed here), the two CH bands have nearly equal intensities (Figure 1; Table 1). Our calculations indicate that $Sc^+(C_2H_2)(^1A_1)$ and $Ti^+(C_2H_2)(^2A_2)$ will behave similarly.

The trend in the red shifts of C−H frequencies of the acetylene complexes, $Fe^+ > Co^+ > Ni^+$, is in line with the metal charges (Table 1) as well as the increase in the CC bond lengths and HCC angles. But it is not directly related to the complexation energies.[8,9] These are nearly the same for the $^nB_1$ Fe^+, Co^+, and Ni^+ states, 44.5 ± 0.3 kcal/mol at B3LYP/6-311+G(3df,2p)+ZPE. Consistent with the metal charges, minor covalent σ-donation and π-back-bonding DCD variations evidently are responsible for the red-shifted band trend and the small structural differences in the Fe, Co, Ni set. $V^+(C_2H_2)$ differs significantly from these three.

We have demonstrated that IR spectroscopy of metal ion−acetylene complexes in the C−H stretch region, combined with DFT computations, provides significant structural insights. The trend of metal charges for Fe^+, Co^+, and Ni^+ π-complexes mirrors the relative C−H stretch red shifts of the acetylene ligands. $V^+(C_2H_2)$ favors the lower multiplicity $^3A_2$ state where back-donation dominates and a three membered ring results. To our knowledge, this is the first spectroscopic confirmation of metallacycle formation in these systems.

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