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Vibrational Progressions in the Valence Ionizations of Transition Metal Hydrides: Evaluation of Metal-Hydride Bonding and Vibrations in (η^5-C_5R_5)Re(NO)(CO)H [R = H, CH_3]

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Received September 10, 2001

Abstract: The first examples of vibrational structure in metal−ligand σ-bond ionizations are observed in the gas-phase photoelectron spectra of CpRe(NO)(CO)H and Cp*Re(NO)(CO)H [Cp = η^5-C_5H_5, Cp* = η^5-$C_5(CH_3)_5$]. The vibrational progressions are due to the Re−H stretch in the ion states formed by removal of an electron from the predominantly Re−H σ-bonding orbitals. A vibrational progression is also observed in the corresponding ionization of the deuterium analogue, Cp*Re(NO)(CO)D, but with lower vibrational energy spacing as expected from the reduced mass effect. The vibrational progressions in these valence ionizations are directly informative about the nature of the metal-hydride bonding and electronic structure in these molecules. Franck−Condon analysis shows that for these molecules the Re−H or Re−D bond lengthens by 0.25(1) Å when an electron is removed from the Re−H or Re−D σ-bond orbital. This bond lengthening is comparable to that of H_2 upon ionization. Removal of an electron from the Re−H or Re−D bonds leads to a quantum-mechanical inner sphere reorganization energy (λ^{QM}) of 0.34(1) eV. These observations suggest that even in these low symmetry molecules the orbital corresponding to the Re−H σ bond and the Re−H vibrational mode is very localized. Theoretical calculations of the electronic structure and normal vibrational modes of CpRe(NO)(CO)H support a localized two-electron valence bond description of the Re−H interaction.

Introduction

The nature of the metal−hydride bond is important to many catalytic, synthetic, and materials processes. Experimentally, photoelectron spectroscopy has proven to be an invaluable tool for obtaining information related to the energetics and nature of metal−ligand bonding in many inorganic and organometallic molecules.[1−6] In addition to providing ionization energies that are important for understanding the valence electronic structure of a molecule, photoelectron spectroscopy reveals vibrational and structural information for the ground and excited positive ion states of the molecule when one or more vibrational progressions are resolved in the ionizations. First-order interpretation of vibrational structure in a photoelectron ionization is straightforward.[7] In the orbital model of electronic structure, a particular positive ion state is obtained from the neutral molecule by removal of an electron from an occupied orbital. Comparison of the vibrational and structural features of the positive ion state to those of the neutral molecule indicates the bonding nature of an electron in that orbital. Qualitatively, if the orbital from which the electron is removed is essentially nonbonding and no geometry change occurs with that ionization, then the most intense ionization will be to the lowest vibrational level in the positive ion. Ionizations to higher excited vibrational quantum levels in the positive ion gain intensity as the minimum-energy structure of the positive ion state becomes increasingly different from that of the neutral molecule. Most often, the geometry change is associated with a bond distance in the molecule. Quantitatively, the difference between the vibrational frequency of the positive ion and the vibrational frequency of the neutral molecule reflects the change in the vibrational force constant caused by removal of the orbital electron, and analysis of the intensity pattern of the vibrational progression measures the change in bond distance caused by removal of the orbital electron.

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10.1021/ja0120227 CCC: $22.00 © 2002 American Chemical Society

Vibrational progressions are commonly observed in the photoelectron spectra of small molecules.[7−9] Vibrational structure is also typically observed in higher resolution laser photoelectron spectroscopy of small inorganic anions or anionic metal clusters,[10−16] but interpretation of these progressions can be difficult because the geometries of the anions under study are not always known. Photoelectron studies of volatile transition metal molecules generally do not show well-resolved vibrational structure. This is due to (a) the low frequencies of vibrations of metal−ligand bonds, (b) the number of vibrational modes that may overlap, and (c) the limitations of the instruments generally used for studies of these molecules.

Although large molecules have a large number of normal vibrational modes, there are effective "selection rules" that lower the number of modes that can lead to observable progressions in an ionization, especially for transition metal complexes. For one, a vibrational mode will give rise to an extensive progression in an ionization only if the energy of geometry relaxation of the positive ion state along the nuclear displacement coordinates of the mode is greater than the vibrational energy spacing of the mode. Metal d orbitals are often somewhat localized, and in these cases only those modes that have substantial nuclear displacements in the region of the metal dominate the vibrational manifold. Even if the particular orbital is delocalized, local electronic symmetry and normal mode symmetry can assist the observation of vibrational structure because the totally symmetric modes normally dominate.[8] Photoelectron spectra of transition-metal containing molecules that have resolved vibrational structure are relatively few to date. Those that have been reported include the metal−metal stretching frequency on the metal−metal δ orbital ionization of $Mo_2(O_2CCH_3)_4$,[17] metal−carbon and carbon−carbon stretching frequencies on the ionizations of metallocenes,[18,19] and metal−carbon and carbon−oxygen stretching frequencies on the metal d ionizations of many metal carbonyls.[20−25] Vibrational structure due to carbon−oxygen stretching has also been observed in the metal core ionizations of metal carbonyls,[6,24,26−28] and the geometry changes observed with these ionizations have been explained in terms of the core equivalent model.[29] With all of these examples, however, there has been no report of resolved vibrational structure in a metal−ligand σ ionization, which would give direct evidence of the bonding nature of this most basic metal−ligand interaction.

Here we report the first observation of vibrational structure in the ionization of a metal−ligand σ-bonding valence orbital, specifically the Re−H σ-bond ionizations of CpRe(NO)(CO)H and Cp*Re(NO)(CO)H and the Re−D σ-bond ionization of Cp*Re(NO)(CO)D [Cp = η^5-C_5H_5, Cp* = η^5-$C_5(CH_3)_5$]. This experimental information is used to evaluate the change in metal-hydride bonding that occurs when an electron is removed from this orbital, and the implications derived from this information with regard to the nature of the metal-hydride bonding in these systems are discussed. One basic question is whether a simple valence bond description, in which the Re−H σ bond is depicted as a localized two-electron bond, can be used to accurately describe the electronic structure of the Re−H bond in these molecules. In contrast, a molecular orbital description would form delocalized linear combinations of metal and ligand orbitals that would mix the Re−H bond with the other Re−ligand bonds and orbitals in the molecule. It might be expected for the low symmetry of these molecules that the σ framework would be extensively delocalized, and, of course, delocalized electronic descriptions are common in organometallic chemistry.[30,31] However, the experimental and computational results presented here indicate that the metal−hydride bond in these systems remains predominantly localized.

Experimental Section

The samples of CpRe(NO)(CO)H,[32] Cp*Re(NO)(CO)H,[33−35] and Cp*Re(NO)(CO)D[35] were prepared according to reported procedures. Photoelectron spectra were recorded using an instrument that features a 36 cm radius, 8 cm gap hemispherical analyzer (McPherson), custom-designed excitation source, sample cells, and detection and control electronics that have been described in more detail.[35] The difference between the argon $^2P_{3/2}$ ionization at 15.759 eV and the methyl iodide $^2E_{1/2}$ ionization at 9.538 eV was used to calibrate the ionization energy scale. The argon $^2P_{3/2}$ ionization also was used as an internal calibration lock of the absolute ionization energy to control spectrometer drift within ± 0.001 eV throughout data collection. During data collection on these molecules the instrument resolution (measured using fwhm of the argon $^2P_{3/2}$ peak) was 0.016−0.022 eV. All data are intensity corrected with an experimentally determined instrument analyzer sensitivity function. The HeI spectrum also was corrected for HeIβ resonance line emission from the source, which is about 3% of the intensity of the HeIα line emission and at 1.869 eV higher photon energy.

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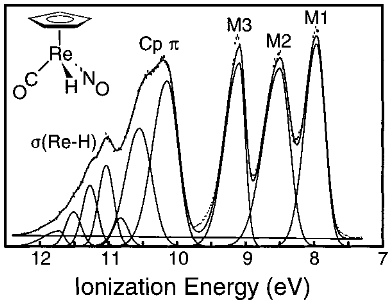

Figure 1. Photoelectron spectrum of CpRe(NO)(CO)H.

All samples sublimed cleanly with no detectable evidence of decomposition products in the gas phase or as a solid residue. The sublimation temperatures were (°C, 10^{-4} Torr, monitored using a "K" type thermocouple passed through a vacuum feedthrough and attached directly to the sample cell) 35−45 for CpRe(NO)(CO)H and 50−60 for Cp*Re(NO)(CO)H and Cp*Re(NO)(CO)D.

In the figures of the data, the vertical length of each data mark represents the experimental variance of that point. The valence ionization bands are represented analytically with the best fit of asymmetric Gaussian peaks as described in more detail elsewhere.[36] The bands are defined with the position, amplitude, halfwidth for the high binding energy side of the peak, and the halfwidth for the low binding energy side of the peak. The number of peaks used in a fit was based solely on the features of a given band profile. The peak positions and halfwidths are reproducible to about ±0.01 eV ($\sim 3\sigma$). The parameters describing an individual Gaussian peak are less certain when two or more peaks are close in energy and overlap.

Theoretical calculations of the electronic structure and normal vibrational modes and frequencies of CpRe(NO)(CO)H were carried out with both the Hartree−Fock and the B3LYP[37] models using program Gaussian98[38] and the effective core potential/double-ζ basis of Hay and Wadt,[39−41] as well as with a number of other basis sets and other density functionals. All methods gave similar results, particularly with respect to the conclusions derived from the vibrational progressions in the ionizations. The figure of the Re−H bond orbital of CpRe(NO)(CO)H is from the B3LYP calculation and is produced with program MOLEKEL[42] using a surface function value of 0.06.

Photoelectron Spectra

The valence ionization spectrum for CpRe(NO)(CO)H from 7.5 to 12.5 eV is shown in Figure 1. The primary character associated with the ionizations in this region can be assigned by comparison to the spectra of other piano-stool molecules,[4] including CpRe(NO)(CO)X (X = halide)[23] and CpRe(NO)(CO)CH_3,[35] and by comparison of spectra collected with HeI and HeII photon sources.[35] The labels assigned to ionizations reflect the primary character of the orbitals from which the ionizations originate as described below. However, it must be remembered that a completely accurate description of these orbitals often includes character from other valence orbitals.

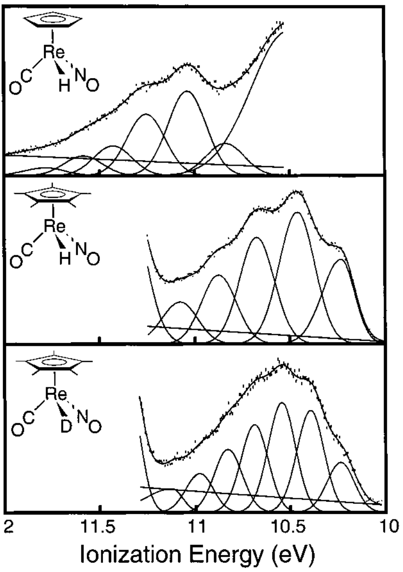

Figure 2. Close-up of the σ(Re−H) and σ(Re−D) ionizations.

In the spectrum of CpRe(NO)(CO)H, there are three relatively sharp ionization bands at 7.96, 8.50, and 9.09 eV labeled M1, M2, and M3 that originate from the predominantly d orbitals of the formally d^6, Re(I) metal center. The spacing of these three ionizations reflects the different π-symmetry interactions of these orbitals with the NO, CO, and H ligands and will be discussed in comparison to other molecules of this class in a separate paper.[35] The ionization near 10.4 eV has a distinctive asymmetric shape with a shoulder on the high binding energy side that is associated with the Cp π ionization of a piano-stool molecule.[20,25] The remaining ionization envelope from 11 to 12 eV is assigned to the Re−H σ-bond ionization. Although this ionization partially overlaps with the Cp π ionization, it is possible to see the unusual shape of the ionization band. The shoulders on the ionization are partially resolved transitions to different vibrational energy levels in the positive ion. This ionization is the focal point for evaluating the Re−H σ bond.

A higher resolution close-up of the Re−H σ-bond ionization of CpRe(NO)(CO)H from 10 to 12 eV is shown in the top of Figure 2. The shoulders on the band are modeled well with symmetric Gaussian bands that have positions and intensities listed in Table 1. The position of the adiabatic ionization is uncertain because the Cp π ionization overlaps with the low binding energy side of the σ(Re−H) band. The position of the most intense peak in the ionization envelope, the vertical ionization energy, is more certain at 11.03 eV. The vertical ionization would appear to correspond to the ν_0(neutral) to ν_1(cation) transition. The vibrational progression has a frequency of 0.223 ± 0.015 eV (1800 ± 125 cm^{-1}), which is lower than the ν(Re−H) for the neutral molecule at 2013 cm^{-1} (Raman, neat). The decrease in frequency is direct evidence for the bonding nature of the Re−H orbital.

The Re−H σ-bond ionization of Cp*Re(NO)(CO)H is shown in the middle of Figure 2. The methylation of the Cp ligand causes the Cp* π ionization of Cp*Re(NO)(CO)H to be destabilized by about 1.1 eV from the Cp π ionization of CpRe-

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Table 1. Positions and Relative Amplitudes of the Vibrationally Resolved Components of the σ(Re−H) and σ(Re−D) Ionizations and the Best Matching Poisson Amplitudes

transition	position (eV)	relative amplitude	Poisson amplitude
CpRe(NO)(CO)H			
ν_0(neutral) → ν_0(cation) (adiabatic)	10.823	350[a]	-
ν_0(neutral) → ν_1(cation) (vertical)	11.034	1000	999
ν_0(neutral) → ν_2(cation)	11.270	750	771
ν_0(neutral) → ν_3(cation)	11.510	426	401
ν_0(neutral) → ν_4(cation)	11.715	189	157
Cp*Re(NO)(CO)H			
ν_0(neutral) → ν_0(cation) (adiabatic)	10.229	639	620
ν_0(neutral) → ν_1(cation) (vertical)	10.459	1000	992
ν_0(neutral) → ν_2(cation)	10.674	769	794
ν_0(neutral) → ν_3(cation)	10.873	453	423
ν_0(neutral) → ν_4(cation)	11.074	212	170
Cp*Re(NO)(CO)D			
ν_0(neutral) → ν_0(cation) (adiabatic)	10.229	426	391
ν_0(neutral) → ν_1(cation)	10.391	928	905
ν_0(neutral) → ν_2(cation) (vertical)	10.544	1000	1046
ν_0(neutral) → ν_3(cation)	10.693	818	806
ν_0(neutral) → ν_4(cation)	10.830	438	465
ν_0(neutral) → ν_5(cation)	10.951	274	215
ν_0(neutral) → ν_6(cation)	11.096	42	83

[a] Partially obscured by other ionization; intensity not included in Poisson distribution analysis.

(NO)(CO)H, but the σ(Re−H) vertical ionization is only destabilized 0.57 eV. Because of the difference in these ionization shifts, the σ(Re−H) ionization for Cp*Re(NO)(CO)H is well separated from the Cp* π ionization, and the vibrational structure in the σ(Re−H) ionization is more clearly observed. The peak at 10.23 eV is the adiabatic ionization for this progression, while the vertical ionization is at 10.46 eV. No hot bands are observed or expected due to the extremely low Boltzmann population of excited vibrational states of the neutral molecule at the temperature at which these data were collected. In terms of the vibrational quantum levels ν_i, the vertical ionization energy corresponds to the ν_0(neutral) to ν_1(cation) transition. The average separation between the peaks is 0.211 ± 0.013 eV (1700 ± 100 cm^{-1}). This frequency is again lower than the Re−H vibrational frequency in the neutral molecule (1994 cm^{-1}, Table 2).

To confirm that the vibrational progressions on the σ(Re−H) ionizations of CpRe(NO)(CO)H and Cp*Re(NO)(CO)H are due to the Re−H stretching frequency, the spectrum of the deuterated analogue Cp*Re(NO)(CO)D was obtained. The σ(Re−D) ionization is shown in the bottom of Figure 2. The valence region photoelectron spectrum of Cp*Re(NO)(CO)D is identical to that of Cp*Re(NO)(CO)H with the exception of the shape of the σ(Re−H) and σ(Re−D) ionizations. Because of the limited amount of sample of the deuteride, the signal-to-noise in this spectrum is not as high as for the hydrides, but the contour of the band nonetheless shows the reduction in vibrational frequency. The σ(Re−D) adiabatic ionization is 10.24 eV, which is statistically the same as that for the hydride analogue. The same adiabatic ionization energy is expected for Cp*Re(NO)(CO)D and Cp*Re(NO)(CO)H because while the absolute zero-point energy of a Re−D bond will be lower than that of a Re−H bond, it will be lower by about the same amount in both the neutral and the excited states leaving the adiabatic transition energy the same. The vertical ionization is now the third peak, which corresponds to the ν_0(neutral) to ν_2(cation) transition. The vibrational energy spacing in the progression is 0.145 ± 0.012 eV (1200 ± 100 cm^{-1}), which is as predicted by the reduced mass effect and is again smaller than the Re−D vibrational frequency in the neutral molecule (1453 cm^{-1}).

Vibrational Analysis

Vibrational Normal Mode and Force Constant. The vibrational information from these spectra can be used to estimate the vibrational force constant and change in equilibrium bond distance when an electron is removed from the σ(Re−H) orbital. Because the energy spacing between the vibrational components of the ionization band is the same within the certainty of the experiment, it is reasonable to assume that the potential well for this state of the positive ion is essentially harmonic within the range of the first several vibrational levels. In this case a classical Hooke's law approximation can be used to describe the energy of the potential well of the positive ion in terms of the vibrational force constant k and the distortion (ΔQ) of the geometry from the equilibrium geometry:

$$E = {}^{1}/_{2}k(\Delta Q)^2 \tag{1}$$

The force constant k is related to the vibrational frequency ν in the positive ion by the following equation:

$$k = 4\pi\mu(\nu)^2 \tag{2}$$

where μ is the usual reduced mass. On the basis of the observed frequencies, the force constants of the Re−H and Re−D modes in the neutral molecules are about 50% larger than the force constants of these modes after ionization from the bonding orbital.

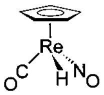
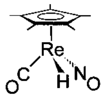
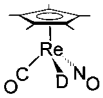
The force constant does not change significantly when H is replace by D, so the ratio of the observed frequencies in the ionizations of Cp*Re(NO)(CO)H and Cp*Re(NO)(CO)D also can be used to determine the ratio of the reduced masses for the vibrational mode in the two molecules:

$$\frac{(\nu_{\mathrm{Re-H}})^2}{(\nu_{\mathrm{Re-D}})^2} = \frac{1.98}{1} = \frac{\mu_{\mathrm{Re-D}}}{\mu_{\mathrm{Re-H}}} \tag{3}$$

The similarity of the ratio of these reduced masses to the ratio of the atomic masses for D and H indicates that the normal vibrational mode is almost entirely restricted to the Re−H and the Re−D stretches. Similarly, the distortion ΔQ must be almost entirely a change in Re−H or Re−D bond distance. On the basis of these equations for harmonic potential wells, the ΔQ could represent either a shortening or a lengthening of the bond distance from the neutral molecule to this positive ion state. The lower vibrational frequencies and force constants in the positive ion states indicate an increase in the equilibrium bond distance, as is naturally expected for ionization from a bonding orbital.

Determination of ΔQ. Two methods are presented for the determination of ΔQ from the ionization information, and the results are summarized in Table 2. The first approach is a simple "vertical" model, which applies most easily when the vertical (most intense) ionization is to a higher vibrational quantum level than that of the ground vibrational level in the positive ion, as is the case here. The vibrational energy of the

Table 2. Vibrational Analysis of σ(Re−H) and σ(Re−D) Ionizations

molecule			
σ bond	Re−H	Re−H	Re−D
ν(neutral)[a]	2013 (neat)	1994 (KBr)	1453 (KBr)
ν(cation)[a]	1800 ± 125	1700 ± 100	1200 ± 100
ν(neutral) − ν(cation)[a]	123	264	253
ΔQ (Å) (classical model)	0.23 ± 0.02	0.24 ± 0.01	0.265 ± 0.01
Franck−Condon analysis			
S	1.56 (3.8%)[b,c]	1.60 (4.2%)	2.32 (6.4%)
ΔQ (Å)	0.240	0.252	0.260
λ^{QM} (eV)	0.35	0.34	0.34

[a] In cm^{-1}. [b] The number in parentheses is the average percent difference between the experimental intensities of the vibrational components and the intensities of the vibrational components as modeled by a Poisson distribution. [c] Intensity of $\nu = 0$ not included in Poisson distribution analysis for CpRe(NO)(CO)H.

positive ion at the vertical ionization is given by

$$E = (\nu_{\max} + {}^{1}/_{2})h\nu \tag{4}$$

where $\upsilon_{\max}$ is the vibrational quantum number in the positive ion for the vertical transition. Equating the energy in eq 1 to the energy in eq 4 and rearranging give the distortion in terms of the vibrational frequency ν and the vibrational quantum number of the vertical level:[8]

$$\Delta Q = \left[\frac{(\nu_{\max} + {}^{1}/_{2})h}{2\pi^2\mu\nu}\right]^{1/2} \tag{5}$$

For CpRe(NO)(CO)H the vertical model approximation gives a Re−H bond lengthening of 0.24 ± 0.01 Å upon removal of an electron. The uncertainty in this value is largely due to the uncertainty in ν, assuming $\upsilon_{\max}$ is chosen correctly. Similar calculations of ΔQ for Cp*Re(NO)(CO)H and Cp*Re(NO)(CO)D, where the observations of $\upsilon_{\max}$ and the leading edge of the ionization are clearer, give values of 0.24 ± 0.01 and 0.265 ± 0.01 Å, respectively.

This vertical model considers the frequency of the vibrational spacing in the cation and the determination of $\upsilon_{\max}$, but does not weigh the relative intensities of all of the vibrational components. The change in equilibrium Re−H bond distance upon ionization from the σ(Re−H) orbital can also be derived from a Franck−Condon simulation of the vibrational profile,[43,44] with the intensity of the vibrational components expected to follow a Poisson distribution as long as the electron kinetic energy dependence of the intensity of the ionization is relatively small.[45]

$$I_n = \frac{S^n}{n!}e^{-S} \tag{6}$$

where I_n is the intensity of the nth vibrational component, and S is a distortion parameter. The distortion parameter is related to the change in equilibrium Re−H bond distance by

$$S = \frac{{}^{1}/_{2}k(\Delta Q)^2}{h\nu} \tag{7}$$

The intensities of the vibrational components of the σ(Re−H) ionizations, listed in Table 1, are found to follow a Poisson distribution within the certainties of the vibrational intensities. The experimentally determined intensity of the adiabatic ionization of CpRe(NO)(CO)H cannot be determined accurately because it is partially obscured by the Cp π ionization and is not included in the analysis. A graph comparing the amplitudes of the vibrational components from the analytical modeling of the ionization data for Cp*Re(NO)(CO)D and the amplitudes of the best fit of a Poisson distribution is shown in Figure 3. The Poisson distributions that best match the experimental relative intensities have S values of 1.56 for CpRe(NO)(CO)H, 1.60 for Cp*Re(NO)(CO)H, and 2.32 for Cp*Re(NO)(CO)D. Using these values of S to solve for ΔQ using eq 7 gives bond distance changes of 0.240 Å for CpRe(NO)(CO)H, 0.252 Å for Cp*Re(NO)(CO)H, and 0.260 Å for Cp*Re(NO)(CO)D. Again, because of the uncertainties in determining the vibrational frequencies in the positive ions, the uncertainties in these distance changes are about ±0.01 Å.

Determination of Quantum-Mechanical Reorganization Energies (λ^{QM}). The distortion parameter (S) is also related to the quantum-mechanical inner sphere reorganization energy (λ^{QM}) by[46,47]

$$\lambda^{QM} = Sh\nu \tag{8}$$

For this case, λ^{QM} is the energy associated with the relaxation of the geometry of the molecular ion caused by removal of an electron from the Re−H σ bond. Using the S values from the Poisson distributions gives inner sphere reorganization energies of 0.35 eV for CpRe(NO)(CO)H, 0.34 eV for Cp*Re(NO)(CO)H, and 0.34 eV for Cp*Re(NO)(CO)D.

Discussion

The observation of resolved vibrational structure in the Re−H σ ionization allows detailed analysis of the effects of removing an electron from the Re−H bond and gives information on the characteristics of metal-hydride bonding. The pictorial summary of this analysis for Cp*Re(NO)(CO)D is shown in Figure 4. This figure is constructed with the correct relative widths of the potential wells, correct scale between the vibrational potential wells of the ground state and the positive ion, and matches the vibrational quantum levels of the ion with the vibrational progression observed in the ionization band. The normal mode potential wells are plotted versus the internal coordinate representing the Re−D bond distance, which is determined to be lengthened by about 0.25 Å in the positive ion. The representations for the rhenium-hydrides are similar, with essentially the same lengthening of the Re−H bond distances in the positive ions. This magnitude of these bond distance increases indicates severe weakening of the Re−H bonds with ionization. For comparison, the bond length of H_2^+ is 0.32 Å longer than the bond length of H_2.[48]

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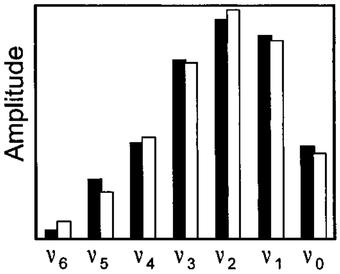

Figure 3. Comparison of the amplitudes of the deconvoluted vibrational components on the σ(Re−D) ionization of Cp*Re(NO)(CO)D, shown in black, with the best matching Poisson amplitudes, shown in white.

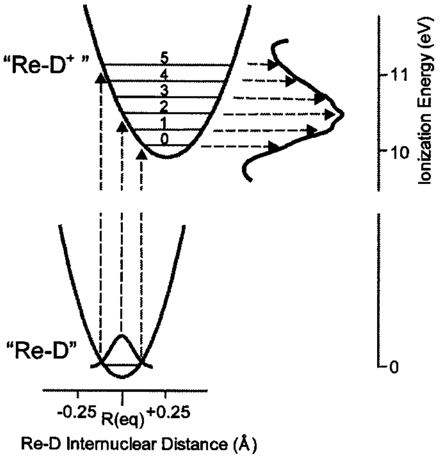

Figure 4. Potential wells for neutral (bottom) and σ(Re−D) ionized Cp*Re(NO)(CO)D (top), and transitions between them. Vertical and adiabatic transitions and the spectrum of the σ(Re−D) ionization (at right) are shown to scale.

The significant geometric distortions upon ionization from the Re−H σ orbitals of these molecules have an associated inner sphere reorganization energy of about 0.34 eV. This value is larger than the inner sphere reorganization energy for organic molecules such as phenanthrene and 1,10-phenanthroline in the gas phase, which have been found to be about 0.1 eV,[47] while the inner sphere reorganization energy of H_2 upon ionization is about 0.6 eV.[49]

As mentioned in the Introduction, the low frequency of vibrations in metal-containing molecules and the number of vibrational modes that may overlap often preclude observation of vibrational structure in ionizations of transition-metal molecules. Nonetheless, ionization from a localized orbital that has a strong energy dependence on a high-frequency vibrational mode may give rise to an observable progression. The results reported here indicate that even for these systems with low molecular symmetry, which might be expected to cause extensive orbital and vibrational mixing, the metal-hydride σ interaction is very localized. In addition to the large bond distance displacement observed upon ionization, other evidence that supports this conclusion includes the strong isotope effect that is observed when deuteride is substituted for hydride and the small effect that changing the ancillary ligand from Cp to Cp* has upon the bond distance displacement. Thus the metal−hydride bond in these systems is well-represented by a localized two-electron orbital valence bond description.

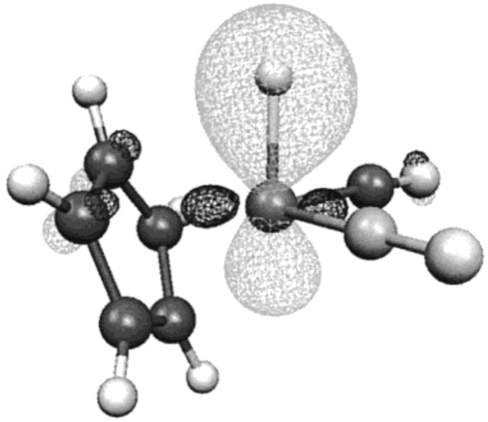

Figure 5. Surface plot of the Re−H σ orbital (HOMO-5) with surface value of ±0.06.

Both density functional and ab initio calculations with a variety of basis sets give results that are in agreement with the localized nature of the Re−H interaction. Figure 5 is an illustration of the Re−H σ orbital from an ab initio calculation. The illustration shows a metal d orbital strongly hybridized toward and mixed with the hydrogen s orbital, and with very little contribution from other regions of the molecule. Ionization from this orbital would be expected to weaken primarily the Re−H bond and produce progressions in any vibrational modes that have a substantial contribution from the Re−H stretch. Frequency calculations by different methods show that a single normal mode in the neutral molecule (at 2100 cm^{-1} ab initio and 2080 cm^{-1} B3LYP density functional) is approximately 99% pure Re−H stretch.

One likely reason that the valence bond model works well for the description of the rhenium−hydride bonds in these systems is that the σ(Re−H) orbital is well separated in energy from the other metal−ligand σ orbitals of the molecule, such that even with a low molecular symmetry orbital mixing is minimal. It is also noted that there is not a direct metal−ligand σ bond in a position trans to the metal−hydride bond, but instead this coordination site involves delocalized bonding to the cyclopentadienyl ring. In turn, the Re−H stretching mode also does not appreciably mix with other vibrational modes of the molecules. The small mass of the hydride or deuteride in relation to the mass of the metal and other ligands favors the localized nature of this vibrational mode.

Organometallic molecules are generally discussed in terms of delocalized electronic interactions, and these concepts have been central to understanding the trends in ionizations of such molecules.[50] Even in discussions of metal coordination chemistry using crystal field theory or other models, which treat the orbitals as largely localized on either the metal or the ligand, it is customary to form symmetry-adapted linear combinations of the ligand orbitals. The results found here show that in certain cases of metal-hydrides a simple two-electron localized orbital valence bond description is most appropriate for the metal−hydride interaction. These molecules demonstrate the orbital and vibrational characteristics that lead to this nature of the metal−hydride bond.

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Conclusions

To summarize, the photoelectron spectra of CpRe(NO)(CO)H, Cp*Re(NO)(CO)H, and Cp*Re(NO)(CO)D exhibit resolved vibrational structures in the σ(Re−H) and σ(Re−D) ionizations due to the Re−H and Re−D stretch in the corresponding cation states. This experimental information can be used to quantitatively evaluate the changes in Re−H bonding and equilibrium bond distance upon removal of an electron. For all three of these molecules, Franck−Condon analysis of the observed vibrational structure indicates that the Re−H or Re−D equilibrium bond distance is lengthened about 0.25 Å upon removal of a σ(Re−H) or σ(Re−D) electron, which corresponds to a substantial weakening of the metal−ligand bond upon removal of an electron and indicates a predominantly localized rhenium-hydride bonding orbital.

Acknowledgment. D.L.L. thanks the U.S. Department of Energy (DE-FG03-95ER14574) and the National Science Foundation (CHE-0078457) for support. J.A.G. thanks the U.S. National Science Foundation and Deutsche Forschungsgemeinschaft (SFB 583) for support.

JA0120227