change is the greatest. Indeed, in that orientation the C₂ hydroxyl group is directed toward the acetamido group (rather than away from it), and the intramolecular interactions stabilizing such an orientation would become more significant as the solvent polarity is lowered.

Evidence supporting such a hypothesis, independent of the present theoretical model, is presented in Table II, which displays a strong correlation between the incremental negative change observed in [θ]₁₀₀ and the solvent dielectric constant.

The proposal that the conformational preferences of substituent groups in these compounds depend on solvent is unexceptional. Determining the precise nature of those preferences, however, is not straightforward. The present work shows that CD, within limits, will reflect differences in the orientation of substituent groups in acetamido sugars. The calculations reported here, although necessarily approximate, direct attention to specific conformational features which are amenable to study by independent means such as NMR.

Conclusions

The theoretical model presented here displays the dependence of acetamido sugar n-α* CD on specific conformational features. It provides an interpretive tool for relating the n-α* CD of glycosaminoglycans to the orientation of constituent acetamido groups. It also allows a qualitative rationalization of several features of the observed solvent dependence of the CD of α-GlcNAC-OMe and β-GlcNAC-OMe, including (1) the stronger solvent dependence of the α-anomer, (2) the positive CD of the α-anomer in strong hydrogen-bond-donor solvents, (3) the negative CD of the α-anomer in other solvents, and (4) the particularly weak CD of the β-anomer in fluorinated alcohols.

Acknowledgment. We thank Professor Lynn Buffington for making her experimental CD data available in advance of publication and for helpful discussions. This work was partially supported by NIH Grant GM24862 and NSF Grant CHE85-09520.

Theoretical Studies of Transition-Metal Hydrides. 4. Comparison of the Transition-Metal Dihydride Ions CrH₂⁺ and MoH₂⁺

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The electronic and geometric structure of two transition-metal dihydride cations, CrH₂⁺ and MoH₂⁺, has been studied theoretically by using generalized valence bond and configuration interaction methods. MoH₂⁺ is found to have two equally favorable geometries: \( R_1 = 1.705 \text{ Å}, \theta_1 = 64.6^\circ \); \( R_2 = 1.722 \text{ Å}, \theta_2 = 112.3^\circ \). These lead to bond energies of \( D_e'(HMO+^-H) \) of 35.1 and 34.7 kcal/mol, respectively, compared with \( D_e'(Cr+^-H) = 33.8 \text{ kcal/mol} \). CrH₂⁺ leads to an open geometry with \( R_2 = 1.635 \text{ Å} \) and \( \theta_2 = 107.5^\circ \). The bond energy is \( D_e(HCr+^-H) = 19.4 \text{ kcal/mol} \) compared with \( D_e(Cr+^-H) = 26.9 \text{ kcal/mol} \).

I. Introduction

The gas-phase activation of hydrocarbons by transition-metal positive ions is an active area of research.\(^{1-12}\) The proposed first step for most of these reactions after initial association is

\[ M^+ + R-H \rightarrow R^- + M^- + H \rightarrow \text{products} \]  (1)

where the initial reaction step involves the insertion of the metal ion into a C-H bond. The initial intermediate thus involves two species \( \sigma \) bonded to the metal ion. There is a growing amount of data, both experimental\(^{13-16}\) and theoretical\(^{14,16} \) dealing with the bond dissociation energies for single species bound to transition-metal ions. Little is known, however, about the geometries of these metal insertion products or the strengths of the second bonds formed to the metals,\(^{1,11,12} \) both of which are important for an understanding of these metal ion reactions.

As a step toward understanding species formed on metal insertion into \( \sigma \) bonds and to compare first and second row metal ions, we investigated the two species CrH₂⁺ and MoH₂⁺. The similarity of the Cr⁺ and Mo⁺ electronic states allows comparison of bonding differences due to orbital size differences of the two metals. The ground-state symmetries, geometries, and bond strengths should be useful in helping to explain differences in the reactivities of the two metal ions. Extension can also be made to predict the geometries and bonding in other transition-metal systems of the first and second transition series.

II. Calculational Details

A. Basis Sets. The basis sets for the present study are identical with those in previous work on metal hydride cations.\(^1\)

For Cr⁺, the all-electron basis involved an optimized valence double \( \zeta \) contraction (1s,10p,5d/5s,4p,2d).\(^{13} \) For Mo⁺, the Ni core was replaced with an ab initio effective core potential\(^{14} \) so that Mo⁺

\footnotesize


has 13 explicitly treated electrons. A valence triple \(\delta\) contraction (5s,5p,4d/4s,4p,3d) of the ab initio basis was used. The hydrogen basis was the uncontracted Dunning/Huzinaga double \(\delta\) basis\(^{15}\) supplemented with one set of \(\pi\) polarization functions (\(\alpha = 0.5\)).\(^{16}\)

**B. Geometry Optimization.** The geometries for the two metal dihydrides were optimized by using a two-step process. The metal–hydrogen bond lengths were fixed at the optimum value found for the diatomic ions (1.602 Å for Cr\(^{2+}\)-H and 1.708 Å for Mo\(^{2+}\)-H) and the \(\pi\)-M–H–\(\pi\) angle was varied to find the optimum angle. The metal–hydrogen bond lengths were then varied at the optimum bond angle for the complex. With this procedure, the optimum bond length for the dihydride complex was found to change only slightly from the value of the monohydride and thus the calculated geometries should be fairly close to the optimum geometries for the two complexes.

**C. Wave Functions.** Four different types of wave function were used in this study of the bonding in CrH\(_2^+\) and MoH\(_2^+\): GVB-PP(2/4), GVB-RCI(2/4), RCI(2/4) \(\times [D_x + D_y + S_{3\pi}]\), and \(D_x + D_y + S_{3\pi}\). These wave functions are described below.

1. **GVB-PP(2/4).** Generalized valence bond calculations allow the two electrons of each bond pair to use different (optimized) one-electron orbitals (generally these optimized orbitals are located primarily on opposite bonding centers), leading to a valence bond (VB)-like wave function of the form

\[
\phi(1) \phi(2) + \phi(\bar{1}) \phi(\bar{2}) (\alpha \beta - \beta \alpha)
\]  

(2)

where \(\phi_1\) and \(\phi_2\) are the optimized one-electron orbitals and \(\alpha\) and \(\beta\) are spin functions. In this simplest GVB wave function, only the two bond pairs are so correlated (with four orbitals total, hence 2/4) and the other electrons on the molecule are calculated self-consistently. Since the two bond pairs have the simple VB form (2), this is referred to as the perfect-pairing (PP) wave function. As one \(\pi\)-M–H bond is broken, the molecule dissociates smoothly to a GVB-PP(1/2) description of MH\(^{+}\) and an H atom.

2. **GVB-RCI(2/4).** The PP wave function does not allow the other spin couplings required to describe the high spin of the separated ions. To include such spin couplings and to allow instantaneous correlation between the electrons of different bond pairs, we allow the two electrons in each bond pair to occupy the two orbitals of this pair in all three possible ways (nine spatial configurations of \(\pi\), \(\pi\), and \(\pi\) character in the metal bonding orbital, \(40.6\%\) and \(55.9\%\) for Cr\(^{2+}\)-H and 50\% for Mo\(^{2+}\)-H).

3. **RCI(2/4) \(\times [D_x + D_y + S_{3\pi}]\).** Starting with the nine spatial configurations of the RCI wave function, we allow all single and double excitations from each metal–hydrogen bond pair to all virtual orbitals. All single excitations from the metal non-bonding valence orbitals (d orbitals) are also allowed. This calculation dissociates smoothly to the RCI(1/2) \(\times [D_x + S_{3\pi}]\) description of MH\(^{+}\) (previously called DCCI-GEOM\(^8\)) and an H atom.

4. **DCI \(\times [D_x + S_{3\pi}]\).** For the metal hydrides, MH\(^{+}\), a calculation level involving single and double excitations from the bond pair simultaneous with excitations from the valence orbitals \(D_x \times S_{3\pi}\) (also called DCCI\(^9\)) was used to determine the metal hydride bond dissociation energies. Using the difference in first and second metal–hydrogen bond energies found in the calculation level described in 3 (for the metal dihydrides) and \(D_x \times S_{3\pi}\) from the DCCI calculations, we estimate \(D_x \times (H^+-\overline{H})\) for a calculation involving simultaneous single and double excitations from both bonds plus single and double excitations from the bond being broken through single excitations from the nonbonding valence orbitals.

### III. Results

Table I presents the main results for both the monohydrides and dihydrides including the optimum geometries, metal orbital hybridizations, and bond dissociation energies. Table II gives information on the configurations, total energies, and bond energies for the various levels of calculation performed on the metal species.

**A. Metal Hydride Cations.** The bonding of H to the first and second row transition-metal hydrides has been described in previous papers.\(^9\) The results obtained for CrH\(^{+}\)+ and MoH\(^{+}\) are summarized here.

1. **CrH\(^{+}\)+.** The optimum bond length for the \(2\Sigma^+\) state of CrH\(^{+}\)+ was found to be 1.602 Å and the vibrational frequency is 1818 cm\(^{-1}\). The calculated bond dissociation energy is \(D_x (Cr^+-H) = 26.9\) kcal/mol which corresponds to \(D_x (Cr^+-H) = 24.3\) kcal/mol. These values are in good agreement with the recent "guided" ion beam experiments of Elkind and Armentrout\(^9\) which give a bond dissociation energy of \(D_x = 27.7 \pm 2\) kcal/mol. Although the Cr\(^+\) ion has a ground-state valence electron configuration of 3\(d^5\), the metal hydride builds in more than 50\% 4s and 4p character in the metal bonding orbital (40.6\% s, 12.5\% p, and 46.9\% d). The bonding orbital of the Cr\(^+\) cation is more diffuse than that for Mo\(^+\) due to the larger amount of s character in the bonding orbital.

2. **MoH\(^{+}\)+.** MoH\(^{+}\)+ is calculated to have an optimum bond length of 1.708 Å and a vibrational frequency of 1826 cm\(^{-1}\). The theoretical bond dissociation energies are \(D_x (Mo^+-H) = 33.8\) kcal/mol and \(D_y (Mo^+-H) = 31.2\) kcal/mol. Ion beam experiments of Elkind and Armentrout\(^9\) which give a bond dissociation energy of \(D_y (Mo^+-H) = 41 \pm 3\) kcal/mol.\(^7\) The lowest lying electronic state of Mo\(^{+}\) is the same as that for Cr\(^{+}\); however, the character of the metal bonding orbital in MoH\(^{+}\) differs markedly from that of CrH\(^{+}\). For MoH\(^{+}\), there is less than 30\% sp character in the metal bonding orbital (19.7\% s, 7.0\% p, and 73.3\% d) compared to the greater than 50\% seen for CrH\(^{+}\).\(^7\) Figure 1 shows the GVB orbitals for the two metal hydrides. Both metal orbitals are seen to be polarized toward the hydrogen atom using atomic p character. The bonding lobe of the Cr\(^+\) orbital is more diffuse than that for Mo\(^+\) due to the larger amount of s character in the bond.
transferred to the Cr+. The bond pairs have an overlap of 0.617.

The Cr+-H bonds are fairly covalent, with about 0.23 electrons per bond and the Cr+ orbital is found to be 40.6% s, 12.5% p, and 46.9% d character, where the 4s character in the metal-hydrogen bond is fixed at 1.602 Å, the optimum value found for OH+. The optimum angle is 107.5°.

Bonding two atoms of hydrogen covalently to 6S Cr+, one is left with three unpaired 3d electrons on the metal. The bonding orbitals can use only combinations of the three orbitals in the yz plane, d\(_{xy}\), d\(_{yz}\), and d\(_{zx}\), leaving unpaired a\(_2\) (xy), b\(_1\) (xz), and a\(_1\) orbitals. This leads to a 4B\(_2\) state of the molecule. For CrH\(^+\) we found a large amount of 4s character in the metal–hydrogen bond and expect the same for CrH\(_2^+\). This requires 3d\(^4\) (5D) character, where the 4s electron must arise from excitation of an electron out of either the 3d\(_2\) or 3d\(_{z^2}\) orbital.

Figure 2 shows the angular energy dependence for C\(_2\) CrH\(_2^+\) with a Cr+-H bond distance of 1.602 Å. The optimum angle found from the GVB-RCI(2/4) calculations is 107.5°. Optimization of the bond lengths at this angle yields a Cr+-H bond length of 1.635 Å. The GVB orbitals for CrH\(_2^+\) are shown in Figure 3 along with the nonbonding (singly occupied) a\(_1\) orbital. The Cr+-H bonds are fairly covalent, with about 0.23 electrons transferred to the Cr+. The bond pairs have an overlap of 0.617.

The hybridizations of metal bonding orbitals are 20.4% s, 9.5% p, and 70.1% d character. Dissociation of CrH\(_2^+\) to CrH\(_+\), Cr\(_+\), and H leads to D\(_a\) (CrH\(_+\)-H) = 4.1 kcal/mol at the GVB-RCI calculation level and D\(_a\) (CrH\(_+\)-H) = 25.3 kcal/mol for the dissociation of the diatomic at the same calculation levels.

Figure 2. Dependence of the CrH\(_2^+\) total energy (at the GVB(2/4) and GVB-RCI(2/4) levels) on the H–Cr+-H bond angle. The Cr+-H bond distance is fixed at 1.602 Å, the optimum value found for CrH\(_+\). The optimum energy is found at 107.5°.
Structure of CrH$_2^+$ and MoH$_2^+$


Figure 3. (a) GVB bond orbitals for the Cr+-H$_2$ bond pair. (b) GVB bond orbitals for the Cr+-H$_1$ bond pair. (c) Cr$^+$ singly occupied $\alpha_1$ orbital which is seen to be mostly d$_z^2$ in character. The Cr$^+$ bond orbitals are found to be 20.4% s, 9.5% p, and 70.1% d.

IV. Discussion

The metal–H$_2$ interaction in CrH$_2^+$ and MoH$_2^+$ differs markedly from that seen in the saturated systems. Group 6 metal complexes involving two hydrogen atoms have been studied in rare gas matrices, rare gas solutions, and organic solvents. Cr(CO)$_3$(H$_2$) has been observed in H$_2$-saturated hydrocarbon solution at room temperature$^{18,19}$ and in Ar matrices at 20 K.$^{20}$ Cr(CO)$_3$(H$_2$), as well as Mo(CO)$_3$(H$_2$) and W(CO)$_3$(H$_2$), has also been produced in liquid xenon (at 70 K) by photolysis of M(CO)$_6$ in the presence of high pressures of H$_2$.$^{19,21}$ IR characterization of these molecules show them to be metal dihydrogen species with intact H–H bonds. $\pi^*$-bonded H$_2$ is also seen in M(CO)$_3$(PR$_3$)$_2$(H)$_2$ ($M = Mo, W; R = Cy, i-Pr$).$^{22}$ Neutron diffraction studies of W(CO)$_3$(P-i-Pr)$_2$(H)$_2$ give the H–H distance as 0.84 Å, slightly larger than for free H$_2$ (0.74 Å). Ab initio Hartree-Fock calculations on the model compound W(CO)$_3$(PH$_2$)$_2$(H)$_2$ yield an H–H distance of 0.79 Å.$^{23}$ Our calculations show that the unsaturated systems form two cova lent metal–hydrogen bonds rather than an $\pi^*$-H$_2$ complex. Thus, even in MoH$_2^+$, with a bond angle of 64.6°, the H–H distance is 1.822 Å.

For CrH$_2^+$ and MoH$_2^+$, we have shown that there are two important metal electronic configurations involved in bonding, d$^0$ and s$d^1$, where the optimum bond involves both d$^0$ and s character on the metal. These two configurations are also found to be important in the bonding of the metal dihydrides. If the optimum bond of a hydrogen atom to a metal is to a d orbital, we expect the optimum bond to require a symmetric (d$_z^2$ or d$_y^2$) orbital to get the largest overlap with the H$_2$. Thus, two

Figure 4. Dependence of the MoH$_2^+$ total energy (at the GVB(2/4) and GVB-RCI(2/4) levels) on the H–Mo$^+-$H bond angle. Mo$^+-$H bond distance is fixed at 1.708 Å and minima are found at 64.6° and 112.3° (GVB-RCI). The energy is seen to increase sharply as the bond angle is opened past 120°. Also shown is the angular energy dependence for d-bonded MoH$^+$ where the use of 5s and 5p functions is restricted. Optimum angles are found at 56.5° and 119.3°. Total energies should not be compared since the Mo$^+$ energy is higher due to the orbital restrictions in the d-bonding case.

strong s bonds to two d orbitals of the d$^2$ metal configuration would require two orthogonal orbitals, each of which is de about its bond axis. This requires bond angles of either 54.7° or 125.3°. Two orthogonal orbitals of de type can be formed in the yz plane by taking linear combinations of the d$_{z^2}$, dyz, and d$^{-1/2}$ atomic orbitals, leading to major axes at an angle of 54.7° (each orbital lying along one of the other’s nodal surfaces).

If the optimum bond of a hydrogen atom to a metal is to an s orbital, the largest amount of s character can be incorporated in two metal–hydrogen bonds by forming two sd hybrid orbitals (e.g., s$_i$ dyz). This would yield an optimum H–M–H angle of 90°. Factors other than optimum hybridization, such as hydrogen–hydrogen repulsion, will modify these bond angles. Examples of s–d and d–d metal hybrid orbitals are shown in Figures 7 and 8. In CrH$_2^+$ and MoH$_2^+$, the four orbitals (s, d$_{z^2}$, d$_{xy}$, and d$_{yz}$) overlapping the two hydrogens are mixed to yield the three orbitals required to describe the three electrons involved in the two metal–hydrogen bonds and the a, nonbonded d electron. The Mulliken population analysis indicates that, for both species, the actual metal hybridization is somewhere in between the sd and dd hybrid limits.

Calculations on ScH$_2^+$ by Alvarado-Swaigood et al. found one minimum on the angular potential surface (optimum angle of 106.7°) and a metal hybridization with approximately 40% sp character. Our GVB-RCI calculations for CrH$_2^+$ (29.9% sp character) hint at a second well at small angle but indicate only one optimum geometry, 107.5°. The MoH$_2^+$ molecule (18.4% or 23.1% sp character at the two optimum geometries) shows the double-well behavior. These observations support the models presented; sd hybridization leads to one minimum near 90° while two bonds to pure de orbitals would lead to a double-well angular potential with optimum bonding at angles near 54.7° and 125.3°. The optimum bond angles for MoH$_2^+$ are 64.6° and 112.3°. Both calculated angles are shifted toward 90° from the pure d–d values. To test whether this shift is due to the 4s and 4p character in the wave function, calculations were performed where the three outermost s and p basis functions were removed. [Other s and p basis functions cannot be removed due to the presence of the 4s and 4p core electrons; thus, some amount of s and p character can still be used in the wave functions.] Figure 4 shows the results of these calculations. Again, a double well in the angular potential is found with the optimum angles of 56.5° and 119.3° shifted toward the values (54.7° and 125.3°) of the d–d model.

The bond in MoH$_2^+$ involves a Mo orbital with 73.3% d character (compared with 46.9% for CrH$_2^+$). If the second metal–hydrogen bond was to a pure d orbital, the two resulting equivalent bonds would have 86.7% d character. The calculational results suggest that the actual values are in between these two results with slightly more s character present in the 112.3° geometry (76.9% d) than in the 64.6° geometry (81.6% d). The shape of the dihydride bond orbitals is thus seen to be quite close to that found for the monohydride with just slightly more d character. For Cr$_2^+$, on the other hand, a second metal–hydrogen bond to a pure d orbital would yield two equivalent bonds each with approximately 73% d character, very close to what is actually calculated.

kcal/mol, leading to second bonds about 14 kcal/mol stronger. In fact, for MoH$_2^+$, we find the second bond is stronger than the first by about 1.3 kcal/mol, suggesting that these two factors are comparable.

Assuming that higher levels of electronic correlation will have the same effect on bond dissociation energies for both the first and second bonds (our calculations support this assumption to about 1 kcal/mol), we can estimate the best theoretical bond energies for the dihydrides using the best theoretical values calculated for the monohydrides. The monohydride values are 33.8 kcal/mol for $D_1$($Mo^{+}$-H), and 26.9 kcal/mol for $D_1(Cr^{+}$-H), leading to overall spin for MoH$^+$ and CrH$^+$ relative to Mo$^+$ and Cr$^+$. Estimates of the energy lost on bonding to Mo$^+$ and Cr$^+$ would be expected to yield decreased exchange penalties. Table III presents the s–d and d–d exchange energies calculated for Cr$^+$ and Mo$^+$. Estimates of the energy lost on bonding to Cr$^+$ are 40 and 26 kcal/mol for the first and second hydrogens, respectively, and for Mo$^+$, approximately 35 and 21 kcal/mol for the first and second hydrogens, respectively, and for Mo$^+$, approximately 35 and 21 kcal/mol for the first and second hydrogens, respectively. Given the significant amount of sd hybridization in the bonds of MoH$^+$ and CrH$^+$, a second bond to a primarily d-like orbital would be expected to be weaker than the first metal–hydrogen bond. On the other hand, little electronic excitation energy is expected to be lost on formation of the second bond and, at the same time, the reduced overall spin for MoH$^+$ and CrH$^+$ relative to Mo$^+$ and Cr$^+$ would be expected to yield decreased exchange penalties. Table III presents the s–d and d–d exchange energies calculated for Cr$^+$ and Mo$^+$. Estimates of the energy lost on bonding to Cr$^+$ are 40 and 26 kcal/mol for the first and second hydrogens, respectively, and for Mo$^+$, approximately 35 and 21 kcal/mol for the first and second hydrogens, respectively.


**TABLE III: Cr$^+$ and Mo$^+$ Exchange Energies**

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<th>Cr$^+$</th>
<th>Mo$^+$</th>
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<td>$\delta$</td>
<td>16.54</td>
<td>20.56</td>
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<tr>
<td>$\delta$</td>
<td>12.51</td>
<td>20.56</td>
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<tr>
<td>$\delta$</td>
<td>17.88</td>
<td>20.56</td>
</tr>
<tr>
<td>$\delta$</td>
<td>9.82</td>
<td>10.91</td>
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*Exchange energy values taken from Hartree–Fock calculations on the atomic ions.*
with hydrocarbons. The bond energies to Cr⁺ are too low to expect insertion into normal C–C or C–H bonds. The presence of a potential minimum at low bond angle for Mo⁺ would also help stabilize the intermediates as the reactant species come together, favoring insertion. Of equal importance with the energetics is the problem of spin conservation. The stable dihydrides have \( S = 1/2 \), whereas the reactants have \( S = 3/2 \). Since a change in total spin is unlikely during a single collision, we expect that the observed chemistry involves either (i) excited \( S = 3/2 \) ions in the beam or (ii) formation of a long-lived complex involving nearly degenerate \( S = 1/2 \) and \( S = 3/2 \) states. The lower excited \( S = 3/2 \) state is 56.7 and 44.0 kcal/mol above the ground state for Cr⁺ and Mo⁺, respectively. The lower value for Mo⁺, along with the increased spin–orbit coupling for the heavier metal, also favors higher reactivity for Mo⁺ vs. Cr⁺.

Current experiments on ion beam studies on the reactions of Cr⁺ and Mo⁺ with alkanes and alkenes[^28] are in agreement with these expectations. While Cr⁺ beams produced by electron impact on Cr(CO)₆ (containing excited state Cr⁺ ions) will react with methane[^28], ground-state Cr⁺ produced by surface ionization yields no exothermic products with alkanes of up to seven carbons in length. On the other hand, ground-state Mo⁺ reacts exothermically with straight chain alkanes, butane or larger, to give metal alkadiene ion products and hydrogen. Mo⁺ is also seen to dehydrogenate alkenes while Cr⁺ only reacts with larger alkenes such as cyclohexene or cyclohexadiene to produce Cr(benzene)[^29]. Cr⁺ insertion into C–H bonds in these cases is facilitated by the double bonds in addition to formation of the M–H and M–C σ bonds.

The current results on Cr⁺ and Mo⁺ systems can also be used for predictions about other metal dihydrides. Bonds of hydrogen and carbon to first row transition metals involve the 4s orbitals. Thus, we expect that the metal dihydrides of the first row will tend to have geometries with bond angles slightly greater than 90°. Also, due to the fact that the second bond must be formed to an orbital having greater d character than for the first metal–hydrogen bond, the second bonds are expected to be weaker than the first (due to nonoptimum metal hybridization). The low-lying electronic states are similar, both having a d electronic configuration in the ground state. However, Mo⁺ has stronger overall bonds dominated by more d-bonding character than Cr⁺, and leading to strong bonding at both small (65°) and large (112°) angles. The larger d–d exchange energies on Cr⁺ and need for s character to produce stronger bonds causes the second Cr⁺–H bond to be very weak. These general trends, along with consideration of the specific metal electronic levels, electron–electron repulsion and exchange energies, and the overlaps resulting from bonding. These effects play a similar role in the dihydrides CrH₂⁺ and MoH₂⁺.

High-Temperature Photoelectron Spectroscopy: A Study of the Alkaline Earth Oxides

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Vacuum ultraviolet photoelectron spectra of vapor-phase SrO and BaO have been recorded and the spectra interpreted by ab initio molecular orbital calculations and Hartree–Fock–Slater calculations. The first band onsets of BaO and SrO have been measured as 6.46 ± 0.07 and 6.60 ± 0.05 eV, respectively, and these lead to upper limits of the dissociation energies, \( D_{0}(\text{in} \text{SrO}(X^2Σ^+) \text{and} \text{SrO}^+(X^2Σ^+)) = 4.37 ± 0.08 \text{ and} 3.36 ± 0.14 \text{ eV} \). Chemiion spectra are presented for the BaO + H₂O and SrO + H₂O reactions.

Introduction

There has been a longstanding interest in the vapor-phase properties of strontium and barium oxides, as these compounds play important roles in a number of areas. For example, it has been shown that BaO is important in understanding the transport of meteor metals to the ground[^12] and barium metal is often

[^28]: Schilling, J. B.; Beauchamp, J. L., submitted for publication.