

change is the greatest. Indeed, in that orientation the C₃ 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 $[\theta]_{\max}$ 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.

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

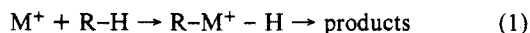
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The electronic and geometric structure of two transition-metal dihydride cations, CrH₂⁺ and MoH₂⁺, has been studied theoretically by using generalized valence bond and configuration interaction methods. MoH₂⁺ is found to have two equally favorable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

I. Introduction

The gas-phase activation of hydrocarbons by transition-metal positive ions is an active area of research.¹⁻⁵ The proposed first step for most of these reactions after initial association is



where the initial reaction step involves the insertion of the metal ion into a C-H bond. The initial intermediate thus involves two species σ bonded to the metal ion. There is a growing amount of data, both experimental^{2,3,6,7} and theoretical,⁸⁻¹⁰ 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,^{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 σ 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. Computational Details

A. Basis Sets. The basis sets for the present study are identical with those in previous work on metal hydride cations.⁸

Conclusions

The theoretical model presented here displays the dependence of acetamido sugar $n-\pi^*$ CD on specific conformational features. It provides an interpretive tool for relating the $n-\pi^*$ 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.

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For Cr⁺, the all-electron basis involved an optimized valence double ζ contraction (13s,10p,5d/5s,4p,2d).¹³ For Mo⁺, the Ni core was replaced with an ab initio effective core potential¹⁴ so that Mo⁺

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TABLE I: Geometries, Orbital Hybridization, Bond Energies for MH⁺ and MH₂⁺

| molecule | state | R _e (M ⁺ -H), Å | θ _e (H-M ⁺ -H), deg | metal orbital hybridization ^a | | | D _e (M ⁺ -H), ^b kcal/mol |
|-------------------------------|-----------------------------|--|--|---|------|------|--|
| | | | | %s | %p | %d | |
| CrH ⁺ | ⁵ Σ ⁺ | 1.602 | | 40.6 | 12.5 | 46.9 | 26.9 |
| MoH ⁺ | ⁵ Σ ⁺ | 1.708 | | 19.7 | 7.0 | 73.3 | 33.8 |
| CrH ₂ ⁺ | ⁴ B ₂ | 1.635 | 107.5 | 20.4 | 9.5 | 70.1 | 19.4 |
| MoH ₂ ⁺ | ⁴ B ₂ | 1.705 | 64.6 | 13.0 | 5.4 | 81.6 | 35.1 |
| MoH ₂ ⁺ | ⁴ B ₂ | 1.722 | 112.3 | 15.4 | 7.7 | 76.9 | 34.7 |

^a Taken from GVB-PP wave functions. ^b From D_σ × S_{M⁺,val} (DCCI) calculations for MH⁺. From the difference between these values and RCI(1/2) × [D_σ + S_{M⁺,val}] (DCCI-GEOM) for MH⁺, the bond energies for MH₂⁺ are extrapolated from the known values from the RCI(1/2) × [D_σ + D_{σ2} + S_{M⁺,val}] calculations.

has 13 explicitly treated electrons. A valence triple ζ contraction (5s,5p,4d/4s,4p,3d) of the ab initio basis was used. The hydrogen basis was the unscaled Dunning/Huzinaga double ζ basis¹⁵ supplemented with one set of p polarization functions (α = 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⁺-H and 1.708 Å for Mo⁺-H) and the H-M⁺-H 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 CrH₂⁺ and MoH₂⁺: GVB-PP(2/4), GVB-RCI(2/4), RCI(2/4) × [D_{σ1} + D_{σ2} + S_{M⁺,val}], and D_{σ1} × [D_{σ2} + S_{M⁺,val}]. 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

$$[\phi_1(1)\phi_r(2) + \phi_r(1)\phi_1(2)](\alpha\beta - \beta\alpha) \quad (2)$$

where φ₁ and φ_r are the optimized one-electron orbitals and α and β 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) (one VB structure), this is referred to as the perfect-pairing (PP) wave function. As one 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 for two bond pairs). This restricted configuration interaction (RCI) approximates the full GVB wave function in which spin coupling is optimized. This calculation level was used for the MH₂⁺ geometry optimizations. For bond energy purposes it dissociates smoothly to a GVB-RCI(1/2) description of MH⁺ and an H atom.

3. **RCI(2/4) × [D_{σ1} + D_{σ2} + S_{M⁺,val}].** 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) × [D_σ + S_{M⁺,val}]

description of MH⁺ (previously called DCCI-GEOM⁸) and an H atom.

4. **D_{σ1} × [D_{σ2} + S_{M⁺,val}].** 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_σ × S_{M⁺,val}, also called DCCI⁸) 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_e(M⁺-H) from the DCCI calculations, we estimate D_e(MH⁺-H) for a calculation involving simultaneous single and double excitations from both bonds plus single and double excitations from the bond being broken times 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.⁸ The results obtained for CrH⁺ and MoH⁺ are summarized here.

1. **CrH⁺.** The optimum bond length for the ⁵Σ⁺ 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_e(Cr⁺-H) = 26.9 kcal/mol which corresponds to D₀(Cr⁺-H) = 24.3 kcal/mol. These values are in good agreement with the recent "guided" ion beam experiments of Elkind and Armentrout⁷ which give a bond dissociation energy of D₀ = 27.7 ± 2 kcal/mol. Although the Cr⁺ ion has a ground-state valence electron configuration of 3d⁵, 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).

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_e(Mo⁺-H) = 33.8 kcal/mol and D₀(Mo⁺-H) = 31.2 kcal/mol. Ion beam experiments of Elkind and Armentrout give a value of D₀(Mo⁺-H) = 41 ± 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⁺. 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.

B. Metal Dihydride Cations. For purposes of discussion, we assume a C_{2v} geometry with the metal ion at the origin, the z axis is the symmetry axis, and the atoms are in the yz plane.

1. **CrH₂⁺.** The ground electronic state of Cr⁺ is ⁶S (3d⁵).¹⁷ The lowest excited state, ⁶D (3d⁴4s¹), lies 1.52 eV higher in energy.

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TABLE II: Energy Information for Molecular and Atomic Species

| species | calcn level ^a | total energy, hartrees | configurations | spin eigenfunctions | bond energy, kcal/mol |
|--------------------------------|--|------------------------|----------------|---------------------|-----------------------|
| CrH ₂ ⁺ | GVB(2/4) | -1042.981 75 | 4 | 4 | -4.6 |
| <i>R_e</i> = 1.635 Å | GVB-RCI(2/4) | -1042.999 26 | 9 | 34 | 4.1 |
| <i>θ_e</i> = 107.5° | RCI(2/4) × [D _{σ1} + D _{σ2} + S _{M⁺,val}] | -1043.043 88 | 1550 | 8472 | 17.8 |
| MoH ₂ ⁺ | GVB(2/4) | -67.736 80 | 4 | 4 | 21.6 |
| <i>R_e</i> = 1.705 Å | GVB-RCI(2/4) | -67.744 83 | 9 | 34 | 24.3 |
| <i>θ_e</i> = 64.6° | RCI(2/4) × [D _{σ1} + D _{σ2} + S _{M⁺,val}] | -67.780 58 | 2636 | 15300 | 35.1 |
| MoH ₂ ⁺ | GVB(2/4) | -67.738 32 | 4 | 4 | 22.8 |
| <i>R_e</i> = 1.722 Å | GVB-RCI(2/4) | -67.745 12 | 9 | 34 | 24.5 |
| <i>θ_e</i> = 112.3° | RCI(2/4) × [D _{σ1} + D _{σ2} + S _{M⁺,val}] | -67.779 87 | 2636 | 15300 | 34.7 |
| CrH ⁺ | GVB(1/2) | -1042.489 81 | 2 | 2 | 8.9 |
| <i>R_e</i> = 1.602 Å | GVB-RCI(1/2) | -1042.493 51 | 3 | 7 | 11.2 |
| | RCI(1/2) × [D _σ + S _{M⁺,val}] | -1042.515 95 | 148 | 444 | 25.3 |
| | D _σ × S _{M⁺,val} | -1042.527 62 | 1862 | 5966 | 26.9 |
| MoH ⁺ | GVB(1/2) | -67.202 65 | 2 | 2 | 19.6 |
| <i>R_e</i> = 1.708 Å | GVB-RCI(1/2) | -67.206 76 | 3 | 7 | 22.2 |
| | RCI(1/2) × [D _σ + S _{M⁺,val}] | -67.225 31 | 258 | 850 | 33.8 |
| | D _σ × S _{M⁺,val} | -67.232 92 | 5234 | 18826 | 33.8 |
| Cr ⁺ | HF | -1041.976 41 | 1 | 1 | |
| | S _σ × S _{val} ^b | -1041.985 50 | 48 | 48 | |
| Mo ⁺ | HF | -66.672 12 | 1 | 1 | |
| | S _σ × S _{val} ^b | -66.679 81 | 135 | 135 | |
| H | HF | -0.499 28 | 1 | 1 | |

^aThese calculations are described in section IIC of the paper. ^bDissociation limit for MH⁺ D_σ × S_{M⁺,val} calculation.

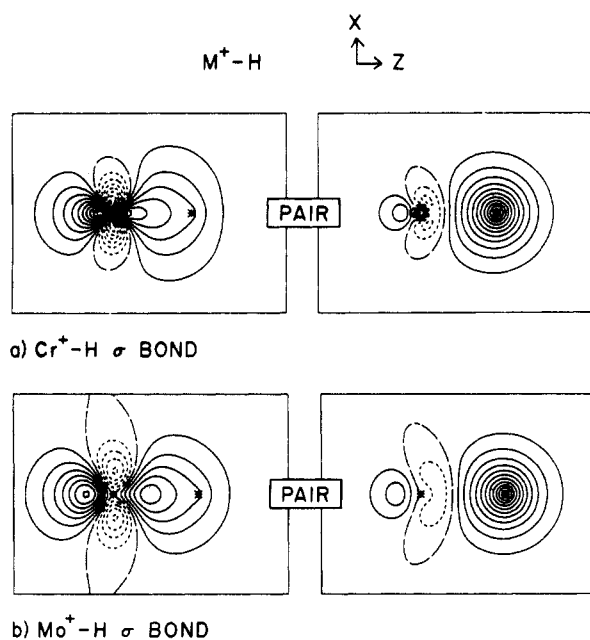


Figure 1. GVB bond orbitals for CrH⁺ (a) and MoH⁺ (b). *R_e*(Cr⁺-H) = 1.602 Å and the Cr⁺ orbital is found to be 40.6% s, 12.5% p, and 46.9% d. *R_e*(Mo⁺-H) = 1.708 Å and the Mo⁺ bond orbital is 19.7% s, 7.0% p, and 73.3%. On all plots long dashes indicate zero amplitude and the spacing between contours is 0.05 au.

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_{z²}, d_{x²-y²}, and d_{yz}, leaving unpaired a₂ (xy), b₁ (xz), and a₁ orbitals. This leads to a ⁴B₂ state of the molecule. For CrH⁺ we found a large amount of 4s character in the metal-hydrogen bond and expect the same for CrH₂⁺. This requires s¹d⁴ (⁶D) character, where the 4s electron must arise from excitation of an electron out of either the 3d_{z²} or 3d_{x²-y²} orbital.

Figure 2 shows the angular energy dependence for C_{2v} CrH₂⁺ 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 CrH₂⁺ are shown in Figure 3 along with the nonbonding (singly occupied) a₁ 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.

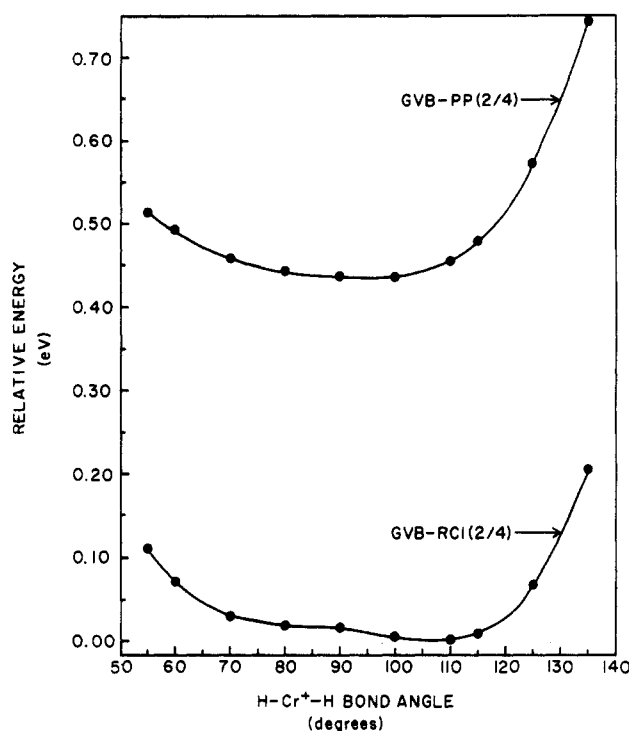


Figure 2. Dependence of the CrH₂⁺ total energy (at the GVB(2/4) and GVB-RCI(2/4) levels) on the H-Cr⁺-H bond angle. The Cr⁺-H bond distance is fixed at 1.602 Å, the optimum value found for CrH⁺. The optimum energy is found at 107.5°.

The hybridizations of metal bonding orbitals are 20.4% s, 9.5% p, and 70.1% d character. Dissociation of CrH₂⁺ to CrH⁺ and H leads to *D_e*(CrH⁺-H) = 4.1 kcal/mol at the GVB-RCI calculation level and *D_e*(CrH⁺-H) = 17.8 kcal/mol at the RCI(2/4) × [D_{σ1} + D_{σ2} + S_{M⁺,val}] level as compared to *D_e*(Cr⁺-H) = 11.2 kcal/mol and *D_e*(Cr⁺-H) = 25.3 kcal/mol for the dissociation of the diatomic at the same calculation levels.

2. MoH₂⁺. The ground state of Mo⁺ is ⁶S (3d⁵).¹⁷ The first excited state is ⁶D (4d⁴5s¹) at 1.59 eV, very close to the splitting for Cr⁺. As with CrH₂⁺, the ground state for MoH₂⁺ is expected to be the ⁴B₂ state. Figure 4 shows the angular energy dependence for the molecule at the two levels of calculation. The MoH₂⁺ molecule differs from its chromium counterpart by exhibiting two distinct minima, at 64.6° and 112.3°, with only a small energy

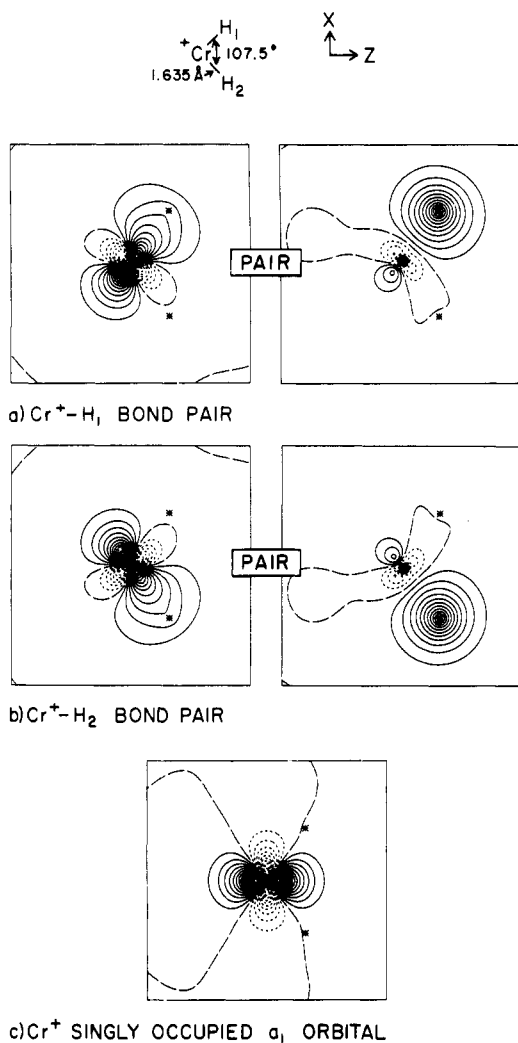


Figure 3. (a) GVB bond orbitals for the Cr^+-H_1 bond pair. (b) GVB bond orbitals for the Cr^+-H_2 bond pair. (c) Cr^+ singly occupied a_1 orbital which is seen to be mostly d_z in character. The Cr^+ bond orbitals are found to be 20.4% s, 9.5% p, and 70.1% d.

barrier between them (transition state at 88.1° with a height of less than 1.5 kcal/mol, probably less than the zero-point energy). Although CrH_2^+ has only one minima (at 107°), it does have some bonding tendency at small angles. Due to the very flat nature of the potential wells observed for both CrH_2^+ and MoH_2^+ , the bending and symmetric stretching vibrations of the two molecules should be quite strongly coupled. Bond length optimization at the two optimum angles gives bond lengths of 1.705 and 1.722 Å, respectively. The bond orbitals for these two geometries are shown in Figures 5 and 6. The bonding is fairly similar for both minima in MoH_2^+ . At 64.6° , the overlap of the bonding orbitals is 0.684, with 0.03 electrons transferred to each hydrogen. The hybridization for the Mo^+ bonding orbitals is 13.0% s, 5.4% p, and 81.6% d character. At the 112.3° geometry, the bond orbital overlaps are 0.687 with 0.06 electrons transferred from Mo^+ to each hydrogen. Here the metal orbital hybridization is 15.4% s, 7.7% p, and 76.9% d. The bond energy, $D_e(\text{MoH}^+-\text{H})$, for the two cases is calculated to be 24.3 and 24.5 kcal/mol, respectively, at the GVB-RCI level and 35.1 and 34.7 kcal/mol, respectively, at the $\text{RCI}(2/4) \times [D_{e1} + D_{e2} + S_{M^+val}]$ level of calculation. The bond dissociation energies for MoH^+ , $D_e(\text{Mo}^+-\text{H})$, at similar levels of calculations, are 22.2 and 33.8 kcal/mol.

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. $\text{Cr}(\text{C}-\text{O})_5(\text{H}_2)$ has been observed in H_2 -saturated hydrocarbon solution

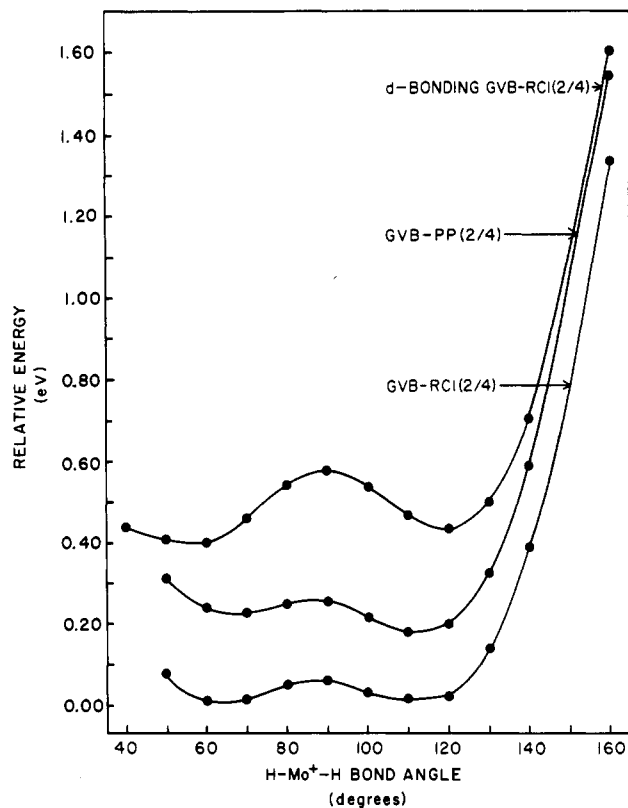


Figure 4. Dependence of the MoH_2^+ total energy (at the GVB(2/4) and GVB-RCI(2/4) levels) on the $\text{H}-\text{Mo}^+-\text{H}$ bond angle. Mo^+-H bond distance is fixed at 1.708 Å and minima are found at 64.6° and 112.3° (GVB-RCI). The energy is seen to increase sharply as the bond angle is opened past 120° . Also shown is the angular energy dependence for d-bonded MoH_2^+ 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.

at room temperature^{18,19} and in Ar matrices at 20 K.²⁰ $\text{Cr}(\text{C}-\text{O})_5(\text{H}_2)$, as well as $\text{Mo}(\text{CO})_5(\text{H}_2)$ and $\text{W}(\text{CO})_5(\text{H}_2)$, has also been produced in liquid xenon (at 70 K) by photolysis of $\text{M}(\text{CO})_6$ 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. η^2 -bonded H_2 is also seen in $\text{M}(\text{CO})_2(\text{PR}_3)_2(\text{H}_2)$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Cy}, i\text{-Pr}$).²² Neutron diffraction studies of $\text{W}(\text{CO})_2(\text{P}-i\text{-Pr})_2(\text{H}_2)$ 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 $\text{W}(\text{CO})_3(\text{PH}_3)_2(\text{H}_2)$ yield an H-H distance of 0.79 Å.²³ Our calculations show that the unsaturated systems form two covalent metal-hydrogen bonds rather than an η^2 - 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^+ and MoH^+ , we have shown that there are two important metal electronic configurations involved in bonding, d^5 and s^1d^4 , where the optimum bond involves both $d\sigma$ 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 or $d\sigma$) orbital to get the largest overlap with the H.²⁴ Thus, two

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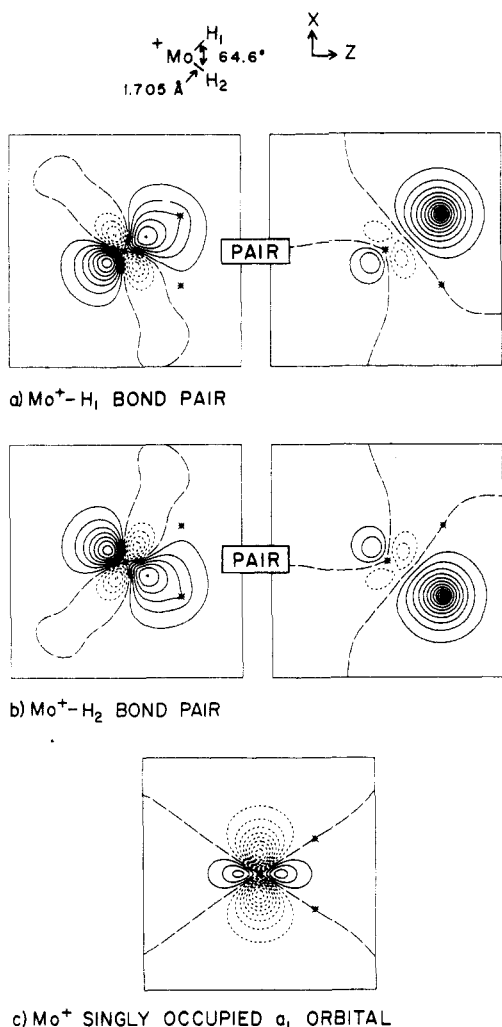


Figure 5. Orbital plots for small-angle MoH₂⁺. (a) Mo⁺-H₁ bond pair orbitals. (b) Mo⁺-H₂ bond pair orbitals. (c) Singly occupied Mo⁺ a₁ orbital showing d_{xy} characteristics. The Mo⁺ bond orbitals are hybridized 13.0% s, 5.4% p, and 81.6% d.

strong σ bonds to two d orbitals of the d⁵ metal configuration would require two orthogonal orbitals, each of which is d σ about its bond axis. This requires bond angles of either 54.7° or 125.3° [Two orthogonal orbitals of d σ type can be formed in the yz plane by taking linear combinations of the d_{z²}, d_{yz}, and d_{x²-y²} 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., $s \pm d_{yz}$). 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 CrH₂⁺ and MoH₂⁺, the four orbitals (s , d_{yz} , $d_{x^2-y^2}$, and d_{z^2}) 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 a₁ 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 ScH₂⁺ by Alvarado-Swaigood et al.¹² 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 CrH₂⁺ (29.9% sp character) hint at a second well at small angle but indicate only one optimum geometry, 107.5°. The MoH₂⁺ molecule (18.4%

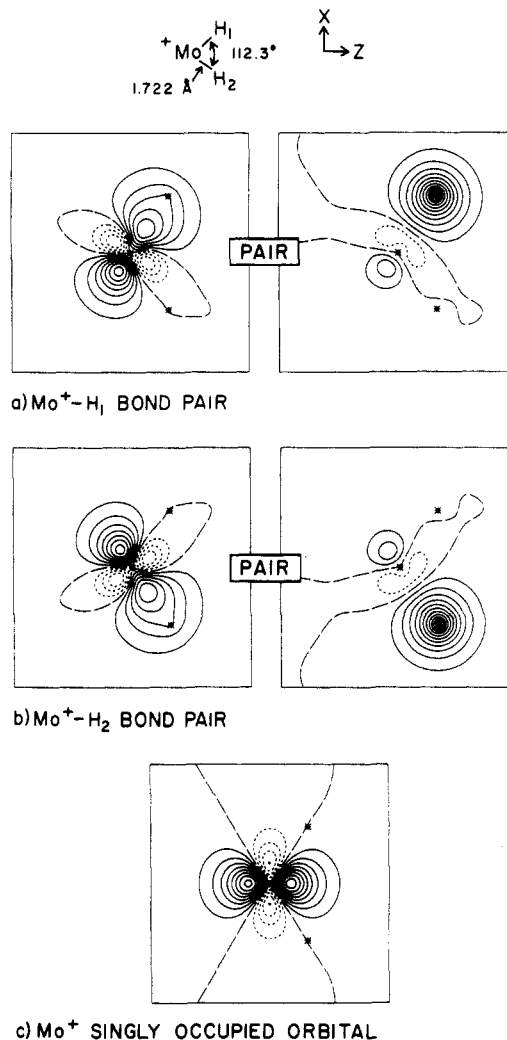


Figure 6. Orbital plots for large-angle MoH₂⁺. (a) Mo⁺-H₁ bond pair orbitals. (b) Mo⁺-H₂ bond pair orbitals. (c) Singly occupied Mo⁺ a₁ orbital showing d_{xy} characteristics. The Mo⁺ bond orbitals are hybridized 15.4% s, 7.7% p, and 76.9% d.

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 minima near 90° while two bonds to pure d σ 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 MoH₂⁺ 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⁺ involves a Mo orbital with 73.3% d character (compared with 46.9% for CrH⁺). 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⁺, 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.

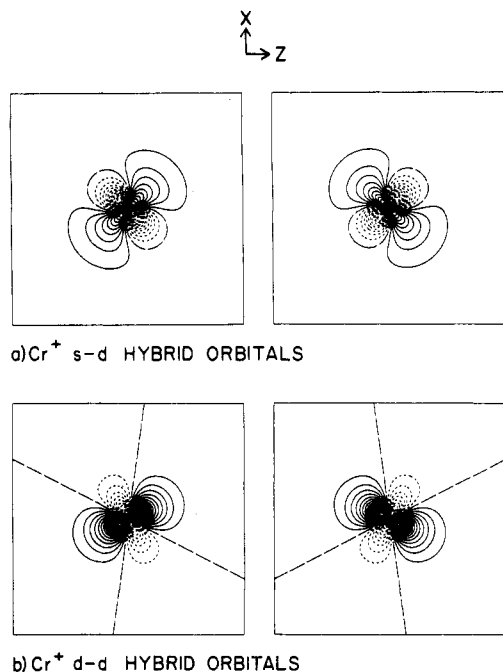


Figure 7. Cr^+ hybrid orbitals. (a) $s-d$ hybrid orbitals which point at 90° from each other. (b) $d-d$ hybrids made up using the d_{z^2} , d_{yz} , and $d_{x^2-y^2}$ orbitals. Each orbital is d_{z^2} -like with respect to its axis, leading to an angle between their major axes of 54.7° . The $s-d$ hybrids are more diffuse than the $d-d$ hybrids due to the larger size of the s orbital.

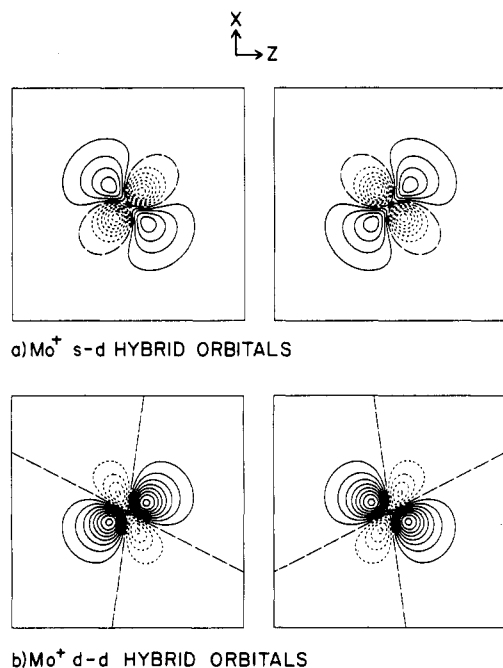


Figure 8. Mo^+ hybrid orbitals: (a) $s-d$ hybrid orbitals pointing at 90° from each other; (b) $d-d$ hybrids made up by using the d_{z^2} , d_{yz} , and $d_{x^2-y^2}$ orbitals. Both orbitals are d_{z^2} -like and the angle between their major axes is 54.7° . The Mo^+ orbitals are seen to be more diffuse than the Cr^+ hybrid orbitals (Figure 7) due to their larger size.

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 CrH^+ are 40 and 26 kcal/mol for the first and second hydrogens, respectively,²⁶ and for Mo^+ , approximately 35 and 21

TABLE III: Cr^+ and Mo^+ Exchange Energies^a

| | Cr^+ | | Mo^+ | |
|--------------------|---------------|-------|---------------|-------|
| | 6S | 6D | 6S | 6D |
| K_{sd} | | 5.12 | | 8.47 |
| K_{dd} | 16.54 | 18.20 | 13.44 | 14.20 |
| $K_{\sigma\sigma}$ | 12.51 | | 10.29 | |
| $K_{\sigma\delta}$ | 20.56 | | 16.59 | |
| $K_{\pi\pi}$ | 17.88 | 19.88 | 14.49 | 15.40 |
| $K_{\pi\delta}$ | 17.88 | 19.88 | 14.49 | 15.29 |
| $K_{\delta\delta}$ | 9.82 | 10.91 | 8.19 | 8.61 |

^a Exchange energy values taken from Hartree-Fock calculations on the atomic ions.

kcal/mol,²⁷ 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 $D_e(\text{Mo}^+-\text{H})$, and 26.9 kcal/mol for $D_e(\text{Cr}^+-\text{H})$, both at the $D_e \times S_{M^+,val}$ level of calculation. This leads to estimated bond energies ($D_{\sigma 1} \times [D_{\sigma 2} + S_{M^+,val}]$) $D_e(\text{Mo}^+-\text{H})$ of 35.1 kcal/mol and $D_e(\text{Cr}^+-\text{H})$ of 19.4 kcal/mol. This can be compared with $D_e(\text{Sc}^+-\text{H}) = 54.7$ kcal/mol and $D_e(\text{ScH}^+-\text{H}) = 51.7$ kcal/mol calculated by Alvarado-Swaisgood et al.¹² Thus, although the bonds in the Sc^+ systems are substantially stronger, the bond strength for the second hydrogen is calculated to be lower than for the first, as seen in CrH_2^+ . As a check on the present calculations vs. those of Alvarado-Swaisgood et al., we have also performed similar calculations on ScH_2^+ . We obtain an optimum geometry with $R_e = 1.762$ Å and $\theta_e = 105.8^\circ$ (compared to 1.745 Å and 106.7°). Bond dissociation energies for the two levels of calculation, $\text{RCI}(2/4) \times [D_{\sigma 1} + D_{\sigma 2} + S_{M^+,val}]$ and $D_{\sigma 1} \times [D_{\sigma 2} + S_{M^+,val}]$, are 51.5 and 52.4 kcal/mol, respectively, in very good agreement with the Alvarado-Swaisgood et al. value of 51.7 kcal/mol.

What kind of predictions can be made about metal ion reactivity based on the geometric and energetic results for the metal dihydrides? The sum of the first and second metal-hydrogen theoretical bond dissociation energies for Cr^+ and Mo^+ are 46.3 and 68.9 kcal/mol, respectively. Since typical C-H or C-C bonds are worth 95–105 and 80–90 kcal/mol, respectively, these results suggest that neither metal in its ground state should insert into bonds of hydrocarbons. As a second estimate, we can use the theoretical differences in first and second bond strengths with the experimental values for the monohydrides to give estimates for the sums of the two bond energies of 48 and 83 kcal/mol for Cr^+ and Mo^+ , respectively. Assuming that the metal-carbon bond is stronger than the metal-hydrogen bond (as reported for some metal species³) and that the metal-carbon bond increases in strength as the carbon chain length increases (better stabilization of metal charge), it is possible that ground-state Mo^+ would react

(26) Starting with the electronic excitation energy (d^5 to s^1d^4) plus the exchange energy lost on bonding to each electronic state, we multiply by the percentage of each metal electronic state determined from the metal hybridization (considering p character as equivalent to s character). Therefore, for the first bond in CrH_2^+ , $2K_{dd}$ or approximately 33.08 kcal/mol of exchange energy is lost upon bonding to the d^5 state (which is present at 46.9%). $2K_{sd}$ or 10.24 kcal/mol of exchange energy and 35.05 kcal/mol electronic promotion energy is lost on bonding to the d^5 state which is present at 53.1%. Using these energies and percentages produces a total energy loss of approximately 39.6 kcal/mol. Exchange energy losses ($1.5K_{dd}$) for the second M^+-H bond amount to approximately 26 kcal/mol.

(27) Using a similar argument as for CrH_2^+ in ref 25. The first bond in MoH_2^+ will lose 73% of the 26.88 kcal/mol lost on bonding to the d^5 state (K_{dd} exchange energy) and 27% of the 36.67 kcal/mol excitation energy and 16.94 kcal/mol $s-d$ exchange energy lost on bonding to the d^5 state. This leads to an overall loss of 34.1 kcal/mol. The second bond loses approximately 21 kcal/mol of exchange energy.

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 $S = 3/2$, whereas the reactants have $S = 5/2$. 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 $S = 3/2$ and $S = 5/2$ states. The lowest excited $S = 3/2$ state is 56.7 and 44.0 kcal/mol¹⁷ 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 experimental ion beam studies on the reactions of Cr^+ and Mo^+ with alkanes and alkenes²⁸ are in agreement with these expectations. While Cr^+ beams produced by electron impact on $\text{Cr}(\text{CO})_6$ (containing excited state Cr^+ ions) will react with methane,²⁹ 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 the reaction with cyclohexene or cyclohexadiene to produce $\text{Cr}(\text{benzene})^+$. Cr^+ insertion into C-H bonds in these cases is facilitated by the complexation due to 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 hybridization and loss of d-d exchange energy). (Experimental results suggest $D(\text{ScH}^+-\text{H})$ to be greater than $D(\text{Sc}^+-\text{H})$ by 3.1 kcal/mol.³⁰) The second row metal ions form bonds principally with their 4d electrons rather than their 5s electrons. We thus expect such second row metal

dihydrides (YH_2^+ to RhH_2^+) to be similar to MoH_2^+ with two possible minima, one at small bond angle ($\sim 60^\circ$). This angle would be expected to vary depending on the electron configuration of the metal. As an example, theoretical calculations by Rappé and Goddard³¹ on Cl_2TiH_2 show that the two hydrogen atoms bond to Ti d orbitals (the two Cl atoms effectively remove the two metal s electrons), leading to a bond angle of 74.9°. The optimum angle for two pure d-like orbitals is 54.7°, while the optimum placement of the two electrons in d orbitals from the standpoint of lowest electron-electron repulsion is $d\sigma d\delta$ with the two electrons in orbitals at 90°. The resultant bond angle is thus a compromise between these two effects. Summarizing we find that for d-bonding situations the ground-state metal electronic configuration plays an essential role in determining the geometry and energetics. Since both bonds to the second row metals are generally to dⁿ configurations, the second bonds should be comparable in strength or possibly stronger than the first (due to a smaller amount of exchange energy being lost, but tempered by nonoptimum metal hybridization).

V. Summary

We find that, for second row transition metals, hydrogen tends to bond to 4d orbitals rather than 5s. This differs dramatically from transition-metal hydride cations of the first row which bond primarily using their 4s orbitals. This difference arises primarily from the difference in size of s and d orbitals where for the second row the d orbitals are more diffuse and closer in size to the large s orbitals. These size differences affect the metal electronic levels, electron-electron repulsion and exchange energies, and the overlaps resulting from bonding. These effects play a similar role in the dihydrides CrH_2^+ and MoH_2^+ . The low-lying electronic states are similar, both having a d⁵ electronic configuration in the ground state. However, MoH_2^+ has stronger overall bonds dominated by more d-bonding character than CrH_2^+ , 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 states, should prove useful in predicting relative bond strengths and geometric structures for other metal species where the metal is σ bonded to two hydrogen or alkyl ligands.

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

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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_0^0 , in $\text{BaO}^+(\text{X}^2\Sigma^+)$ and $\text{SrO}^+(\text{X}^2\Sigma^+)$ of 4.37 ± 0.08 and 3.36 ± 0.14 eV. Chemielectron spectra are presented for the $\text{BaO} + \text{H}_2\text{O}$ and $\text{SrO} + \text{H}_2\text{O}$ 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 ground¹⁻³ and barium metal is often

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