The electronic spectrum of manganese hydride

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This increases S_0 by increasing the residence time of N_2 on the W(110), and a long residence time leads to multiple attempts at surmounting the narrow activation barrier region in this system,[2] which is also the cause of total energy scaling. The connection between the unusual dependence of S_0 on j and E_i is thus traceable to the same feature of the reactive PES, namely the narrow activation barrier.

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Walter J. Balfour
Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

The diatomic hydrides of the transition metals are of interest not only because these metals are valuable hydrogenation catalysts and the M–H molecule represents the simplest such metal–hydrogen bond, but also for astrophysical and theoretical reasons. However, while their optical spectra are readily observed in absorption and emission, analysis of these spectra has proved to be exceedingly difficult due to the complex nature of the patterns displayed. Systems which possess unpaired d electrons can give rise to many close-lying and interacting electronic states of large orbital angular momentum and high spin multiplicity.

Manganese hydride is a typical case in point: of six electronic systems reported in the literature, [1,2,3] near 416, 450, 480, 566, 847, and 939 nm, respectively, only the 566 nm system has yielded to rotational analysis, as a $^7\Pi$–$X\,^7\Sigma$ transition.[3] Complementary to these conventional studies, some details on the electronic energies and characteristics of transition–metal hydride states have been derived from elegant laser photoelectron spectroscopy experiments on the corresponding negative ion species by Lineberger and co-workers.[4,5] In particular, they located a MnH state of quintet multiciplicity lying approximately 1725 cm^{-1} above the ground $^7\Sigma$ state. The state was originally inferred to be of $^5\Delta$ symmetry, but the more recent observations favor a $^5\Sigma$ interpretation with the authors concluding that "a definitive assignment awaits a rigorous optical spectroscopic analysis." The purpose of this Communication is to record that such an analysis confirms the $^5\Sigma$ assignment and has characterized two additional electronic states of quintet multiplicity.

The MnH/D spectrum from Mn + H$_2$ or Mn + D$_2$ was recorded in the region 11 250–12 250 cm^{-1} in thermal emission using a King furnace at ~1850 K and a Bomem DA3.002 Fourier transform spectrometer. The apodized resolution was set at the estimated Doppler linewidth of 0.04 cm^{-1}. The low dispersion spectrum consists of two wings of intensity, one on either side of a minimum near 11 800 cm^{-1}. When examined in detail the rotational structure shows ten branches of appreciable intensity, which form five pairs of associated R and P branches typical of a $^5\Sigma$–$^5\Sigma$ transition. The lines of the F_1 and F_5 spin components are perceptibly broader due to unresolved nuclear hyperfine coupling attributable to interaction with the ^{55}Mn nucleus [$I = 5/2$, $\mu_n = 3.444$ n. m. (nuclear magneton)]. The upper $^5\Sigma$ state is occasionally perturbed at high J values. A linear least squares fit to average second rotational combination differences gives the following MnH constants for $v = 0$ vibrational levels:

lower $^5\Sigma$ state:

$B = 6.3444(0.0003)$ cm^{-1}; $r = 0.1638$ nm,

$D = 3.95(0.01) \times 10^{-4}$ cm^{-1},

upper $^5\Sigma$ state:

$B = 6.2162(0.0005)$ cm^{-1}; $r = 0.1655$ nm,

$D = 3.27(0.02) \times 10^{-4}$ cm^{-1},

where the bracketed numbers are the standard deviations.

The successful rotational analysis of the 847 nm, infrared system has opened the door to progress in understanding the more complex structure of the 480 nm system, for combination differences confirm that the 847 and 480 nm systems have the same lower electronic state. That this $^5\Sigma$ state lies close in energy to the ground state as suggested by the photoelectron data is reinforced by the occurrence of the 480 nm system in absorption.

Part, if not all, of the very dense structure in the MnH

spectrum around 20 900 cm^{-1}, can be attributed to a $^5\Pi$–$^5\Sigma$ transition, where the $^5\Pi$ state (MnH) has B_0 = 6.075(0.001) cm^{-1}, i.e., $r = 0.1674$ nm, and D_0 = 3.58(0.02)×10^{-4} cm^{-1}. Further detailed study will be required to establish the spin–orbit and Λ-doubling parameters of the $^5\Pi$ state and the spin splitting parameters of the $^5\Sigma$ states. Such research is already underway.[6]

Bonding in the transition metal hydrides has been treated theoretically by Bauschlicher and associates.[7,8] Qualitatively, in the high spin $^7\Sigma$ ground state the bond arises from the Mn $3d^5 4s^2(S)$ ground configuration, with one $4s$ electron forming a sigma bond to hydrogen and the other becoming a σ^* electron, yielding $d^5\sigma^2\sigma^{*1}$, whereas, in its low spin counterpart, the low-lying $^5\Sigma$ state, the bond has a substantial contribution from Mn $3d^6 4s^1$, yielding $d^6\sigma^2$. In this way the stronger bond of the $^5\Sigma$ over $^7\Sigma$ may be understood.

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Cu₂⁺ vibronic states at 0–1.4 eV from multiphoton ionization–photoelectron spectroscopy

Andrew D. Sappey, J. E. Harrington, and James C. Weisshaar
Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706

Laser vaporization sources[1] of gas phase transition metal clusters permit rapid progress in the *chemistry*[2] of both neutral (M_n) and cationic (M_n^+) species with $n \lesssim 30$. Yet our understanding of the electronic and vibrational *structure* of such species[3] remains primitive, in spite of recent progress in optical,[4] ESR,[5] and photoelectron[6] spectroscopies. A long term goal must be the correlation of size-specific metal structure with reactivity.[7] Cations are well suited to this goal since they permit mass selection of reactants. However, no spectroscopic data exist even for diatomic transition metal cations.

In this work, we use photoelectron spectroscopy to provide new information about the low-lying states of one such ion, Cu₂⁺. Viewed simply, Cu₂ and Cu₂⁺ are transition metal analogs of H₂ and H₂⁺. Just as Cu₂ has served as a benchmark for closed-shell transition metal species, Cu₂⁺ can provide a relatively simple system for calibration of all-electron[8] and core-pseudopotential[9] theoretical techniques as applied to *open-shell* metal species. The $^1\Sigma_g^+$ ground state of Cu₂ is fairly well described[10] by the single $4s\sigma$-bonded electron configuration [core] $(3d\sigma_g)^2 (3d\pi_u)^4 (3d\delta_g)^4 (3d\delta_u)^4 (3d\pi_g)^4 (3d\sigma_u)^2 (4s\sigma_g)^2$. Removal of one s or d electron gives rise to seven Cu₂⁺ molecular terms, all likely chemically bound: the "s-hole" $^2\Sigma_g^+$ term (one-half $4s\sigma$-bond, H₂⁺ ground state analog) and six "d-hole" terms $^2\Sigma_{g,u}^+$; $^2\Pi_{g,u}$; and $^2\Delta_{g,u}$. The d-hole terms correlate to excited state Cu⁺ + Cu asymptotes; formally, these have a full $4s\sigma$ bond and a half-bond or a half-antibond of either σ,π, or δ symmetry. Single configuration self-consistent field (SCF) calcula-

tions[11] found the s-hole $^2\Sigma_g^+$ term to be the ground state, with various localized ($C_{\infty v}$ electronic symmetry) d-hole terms at an estimated 2.0 eV excitation energy.

The experiment uses one-color, resonant two-photon ionization (R2PI) to selectively ionize Cu₂ from a skimmed supersonic beam of cold Cu$_n$ species created by laser vaporization and expanded in He.[12] Time-of-flight analysis yields the photoelectron spectrum (TOF-PES).[12] A frequency doubled, pulsed dye laser (260–267 nm, 5 ns FWHM) ionizes Cu₂ via various v'–0 vibrational bands of Smalley's System V resonant state,[13] accessing Cu₂⁺ states up to 1.4 eV.

Figure 1 shows segments of the PESs resulting from 0–0, 1–0, and 2–0 R2PI. The threshold of 7.899 ± 0.005 eV above the Cu₂ ground state agrees with the ionization energy inferred from R2PI band intensities.[13] At higher ion energy, we resolve two excited state vibrational progressions with origins at 1.143 and 1.256 eV; both are well described by $\omega_e^+ = 252 \pm 17$ cm^{-1} and $\omega_e x_e^+ = 1 \pm 3$ cm^{-1}. The frequency is slightly smaller than that of the single-bonded Cu₂ ground state ($\omega_e'' = 266$ cm^{-1}).[14] Ion←neutral resonant state Franck–Condon factors (FCFs) model all three intensity envelopes reasonably well[15] (dots in Fig. 1). The 898 ± 13 cm^{-1} separation is a sensible spin–orbit splitting for a $3d$-hole $^2\Pi$ state.[16]

In the range 0–1 eV above threshold, we observe a dense set of at least 50 moderately well-resolved vibronic states. Within experimental uncertainty, the first 26 band positions can be fit as a *single vibrational progression* having $\omega_e^+ = 187 \pm 8$ cm^{-1} and $\omega_e x_e^+ = 0.7 \pm 0.2$ cm^{-1}. This

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