

Effect of kinetic and electronic energy on the reactions of Cr^+ with H_2 , HD, and D_2

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The reactions of atomic chromium ions with H_2 , HD, and D_2 are examined using guided ion beam tandem mass spectrometry. The ground electronic state (6S) is found to react inefficiently. The thresholds of these data are analyzed to yield a 0 K bond dissociation energy for CrH^+ of 1.37 ± 0.09 eV (31.6 ± 2.0 kcal/mol). In the reaction of Cr^+ (6S) with HD, formation of the metal deuteride ion is strongly favored over that of the metal hydride ion in the threshold region but not at higher energies. These results indicate that Cr^+ (6S) reacts largely via an impulsive mechanism. No evidence for reaction of Cr^+ (6D), the first excited state, is found but higher lying excited states, 4D and 4G (produced by electron impact), are found to react at their thermodynamic threshold. In reaction with HD, these states produce CrH^+ preferentially by a factor of 2–4 over CrD^+ . The differences in reactivity among these states can be explained by using simple molecular orbital concepts which have been developed for other atomic transition metal ions.

INTRODUCTION

The past decade has seen extensive investigations of the reactivity of the first row transition metal ions. Chromium has escaped the intense scrutiny to which Fe^+ , Co^+ , and Ni^+ have been subjected because it is unreactive. This has been attributed to the fact that the Cr^+ (6S , $3d^5$) ground state makes weak covalent bonds because of its stable half-filled shell. This explanation further suggests that excited states of Cr^+ should be much more reactive than the ground state. This has been nicely documented by Ridge and co-workers¹ and by Halle *et al.*² who have shown that electronically excited Cr^+ reacts efficiently with H_2 and with methane. These studies make it clear that, for the chromium system, electronic excitation is more effective than translational excitation in promoting reaction.

Recently, we have published several reports on the effect of electronic excitation on the gas phase reactions of first row transition metal ions with H_2 and its isotopic analogs.^{3–6} These studies reveal that the mechanisms and efficiencies of these reactions depend strongly on the electronic state of the metal ion. Work on several states of V^+ ,³ Mn^+ ,⁴ Fe^+ ,⁵ Co^+ , Ni^+ , and Cu^+ ⁶ have shown four categories of reactivity which correlate with the electron configuration of the metal ion. These are (1) $3d^n$ ($n < 5$) which react fairly efficiently with H_2 and yield comparable amounts of MH^+ and MD^+ in reaction with HD; (2) $3d^n$ ($n > 5$) which react efficiently with H_2 and yield about 3–4 times more MH^+ than MD^+ in reaction with HD; (3) low-spin $4s3d^{n-1}$ which react like group #2; and (4) high-spin $4s3d^{n-1}$ which react inefficiently with H_2 and, in the reaction with HD, exhibit marked isotope effects, greatly favoring the production of MD^+ over MH^+ in the threshold region.

In trying to explain *why* these differences in reactivity exist, we have relied heavily on a consideration of the molecular orbital diagram in Fig. 1. As a metal ion approaches H_2 ,

the outermost atomic orbital on the metal, the $4s$, begins to interact with the filled σ_g orbital of H_2 . If the approach is along the C_{2v} axis, bonding and antibonding MOs ($1a_1$ and $4a_1^*$) are formed, Fig. 1. This is the dominant interaction at chemical distances. Since two electrons are contributed by the σ_g orbital, the occupation of the $4s$ becomes a deciding factor in the course of the reaction. If empty (as for group #1 and #2 ions), the $4a_1^*$ orbital remains unoccupied and the metal can approach more closely and reaction ensues. If the $4s$ is occupied (groups #3 and #4), the $4a_1^*$ is occupied and a repulsive interaction occurs. This is relieved by an approach along the $C_{\infty v}$ axis where the $4s$ orbital can interact with the unoccupied σ_u orbital on H_2 . Much like the $\text{H} + \text{H}_2$ reaction, the $4s$ orbital now correlates with a largely nonbonding orbital having a node in the middle of the $\text{M}^+ - \text{H} - \text{H}$ intermediate and eventually to a $1s$ electron on the H atom product. For low-spin $4s3d^{n-1}$ ions, favorable bonding interactions between the $3d$ electrons and the trailing H atom can occur. Thus, the group #3 ions are more reactive than high-spin $4s3d^{n-1}$ ions which have repulsive interactions between the $3d$ electrons and this H atom.

We have contended that the determining factor for distinguishing between group #1 and group #2 is the occupancy of the $3d\sigma$ orbital. Since this orbital has the same symmetry as the $4s$, its interactions with H_2 are comparable. On the left-hand side of the first transition metal series (group #1), the $3d\sigma$ and thus the $3a_1$ MO can be left unoccupied and the metal ion can insert into H_2 in C_{2v} symmetry. On the right-hand side (group #2), all low energy $3d^n$ configurations must occupy the $3d\sigma$ orbital and thus the $3a_1$ MO in C_{2v} symmetry. This interaction apparently results in a preference for a direct mechanism.

Cr^+ occupies a unique position in the first row, the center. This results in low-lying electronic states of Cr^+ which belong to all four groups. The ground state is a $3d^5$ configuration which naturally occupies the $3d\sigma$ orbital and is therefore expected to act as a member of group #2. From the

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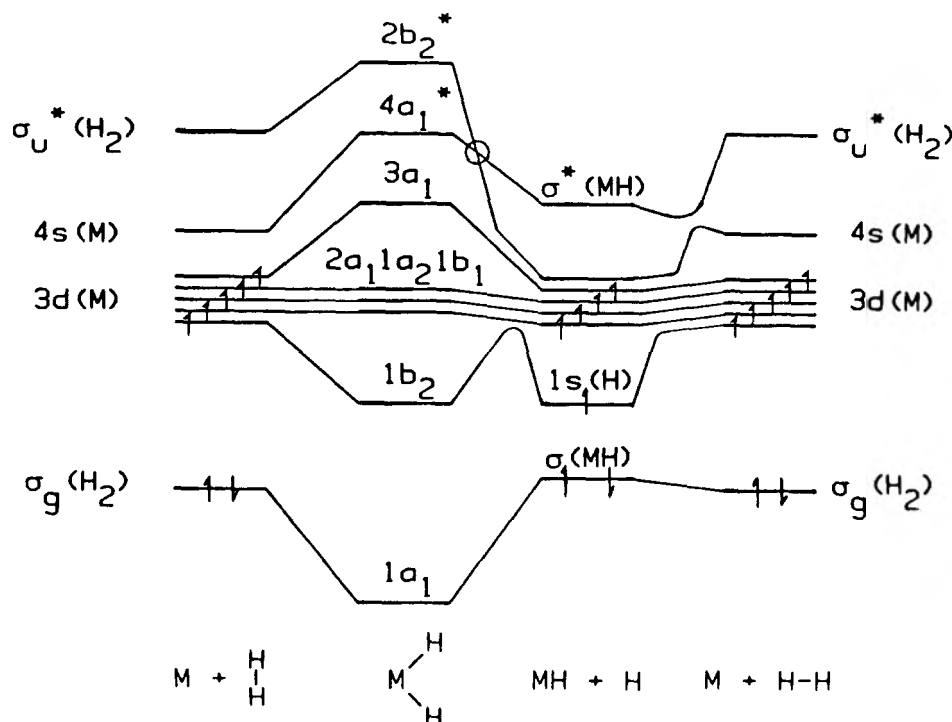


FIG. 1. Qualitative molecular orbital diagram for the interaction of a metal with H₂ in C_{2v} symmetry (left-hand side) and C_{∞v} symmetry (right-hand side). The electron populations shown are for ground state Cr⁺(⁶S) reacting with H₂(¹Σ_g⁺) to form ground state products, CrH⁺(⁵Σ) + H(²S). The circle shows a crossing which is avoided in C_s symmetry.

electron configurations listed in Table I, the lowest three excited states (⁶D, ⁴D, and ⁴G) should behave as group #4, #3, and #1 ions, respectively. Despite the fact that these categories have been extremely useful in qualitative descriptions of the reactivity of many electronic states of several ions, the present study finds that this categorization is incomplete (although not incorrect). While the reactivity of the excited states is found to be as predicted, the experimental evidence conclusively shows that Cr⁺(⁶S) does not behave as a group #2 ion. This unanticipated behavior is shown to be unique among the first row metals and allows a further characterization of the most important features in the interactions of transition metals with hydrogen.

EXPERIMENTAL

The ion beam apparatus used in these experiments has been described previously.⁷ The production of chromium ions is detailed below. The ions are extracted from the source, accelerated, and focused into a magnetic sector for mass analysis. For these experiments the ⁵²Cr isotope (83.76% natural abundance) is used. The mass selected ion beam is decelerated to a selected kinetic energy and focused into an octopole ion trap which utilizes rf electric fields to trap ions in the radial direction. The ions pass through a collision chamber containing the reactant gas at pressures in the range of 0.2–1.0 mTorr as measured by an MKS Baratron capacitance manometer. This is sufficiently low that reactions due to multiple ion–molecule collisions are improbable. The octopole ion guide ensures efficient collection of all ionic products and transmitted reactant ions. After exiting the reaction cell, these ions are extracted from the octopole, focused into a quadrupole mass filter for mass analysis, and detected using a scintillation ion counter and standard ion counting techniques. A DEC MINC computer

system controls the reaction conditions and data collection. Raw ion intensities are converted into absolute reaction cross sections as described previously.⁷

Ions are produced in two different sources. In the surface ionization (SI) source, CrO₂Cl₂ vapor is directed at a rhenium filament which is resistively heated to 2200 ± 100 K, as measured using optical pyrometry. The vapor decomposes on this filament and chromium ions are produced by surface ionization of the resulting Cr atoms (IP = 6.766 eV).⁸ If we presume that the Cr reaches equilibrium at the filament temperature before desorption, the electronic state distribution of the beam produced by SI should have a Maxwell–Boltzmann distribution, Table I. Previous studies^{3–6,9} in our lab on other systems indicate that this is a reasonable approximation.

A second method used to produce Cr⁺ is electron impact (EI) ionization of CrO₂Cl₂ and Cr(CO)₆. Ions are formed when the electron energy (E_e) exceeds the appearance potential of Cr⁺ from CrO₂Cl₂ (19.15 ± 0.07 eV)¹⁰ and Cr(CO)₆ (15.36 ± 0.03 eV).¹¹ A distribution of Cr⁺ states is produced and can be altered by varying E_e.

Ion energies in the laboratory frame, E(lab), are converted to energies in the center of mass (c.m.) frame using the expression E(c.m.) = E(lab) × m/(m + M), where m and M are the masses of the reactant gas and ion, respectively. Retarding field energy analysis is used to determine the absolute zero and distribution of the ion beam kinetic energy. This analysis is achieved by sweeping the dc bias of the octopole trap through the nominal ion energy zero, the difference between this bias and the ion source voltage. The derivative of this retardation curve is nearly Gaussian with a width characteristic of the beam spread and a peak taken to be the energy scale origin. Because this energy analysis region and the reaction zone are physically the same, ambiguo-

ities in the analysis resulting from contact potentials, space charge effects, and focusing aberrations are minimized. The true ion beam energy zero can be measured with an absolute uncertainty of <0.1 eV lab.⁷ This introduces an energy uncertainty of ≤3, 5, and 7 meV c.m. for the H₂, HD, and D₂ reactions, respectively. The ion beam energy distributions produced by SI and by EI are found to have a typical FWHM of 0.7 eV lab (26, 38, and 50 meV c.m. for the H₂, HD, and D₂ reactions, respectively). The effect of the thermal motion of the gas in the reaction cell contributes a much larger uncertainty to the collision energy.^{7,12} The resultant energy distribution effectively broadens any sharp features in the excitation function. Both this effect and the ion beam energy distribution are taken into account when analyzing the experimental results.⁷

CrO₂Cl₂ and Cr(CO)₆ are obtained from Alfa and are used without further purification except for multiple freeze-pump-thaw cycles. HD has been prepared by standard procedures.¹³ Purity of >96% HD was confirmed by mass spectrometric analysis. Impurities are primarily H₂ and D₂ in nearly equal amounts as confirmed by Raman spectroscopic analysis.

RESULTS

Cr⁺(SI) + H₂ and D₂

Shown in Fig. 2 is the experimental excitation function for reaction (1) where Cr⁺ has been produced by surface ionization (SI):

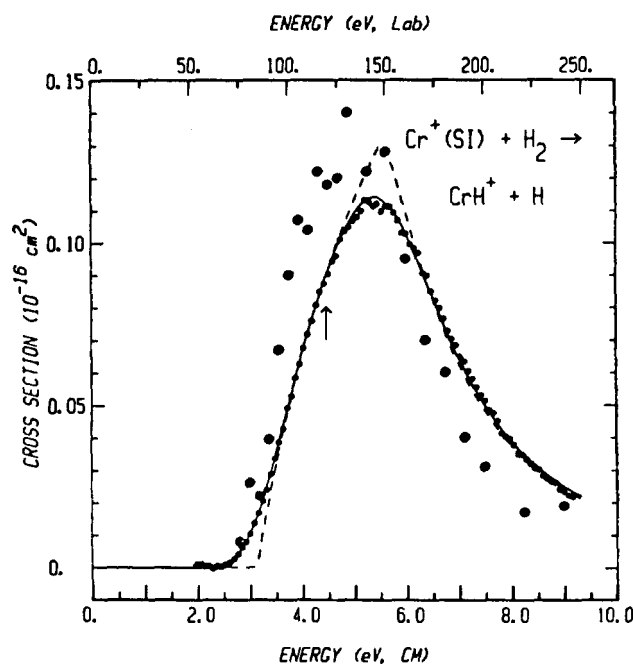


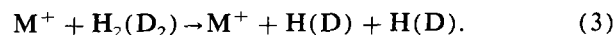
FIG. 2. Cross sections for the reaction of Cr⁺ produced by surface ionization (SI) with H₂ as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). The small points show the present data while the large points show the data from Ref. 2 on the same absolute scale. The data are compared with a line-of-centers model (broken line) and its convolution (full line) over the experimental energy distributions. At energies above 5.5 eV, the product dissociation model discussed in the text is included. The arrow indicates the bond dissociation energy of H₂ at 4.48 eV.



The general shape of the cross section is fairly typical for an endothermic reaction. It rises from an apparent threshold of about 2.5 eV to a maximum of $\approx 0.11 \text{ \AA}^2$ at about 5.5 eV before falling off at higher energies. Results for reaction (2) are similar in shape but are about 20% smaller than the H₂ results:



This difference is within the experimental uncertainty but is systematically observed. Two unusual aspects of these excitation functions can be noted. One, the cross sections are significantly smaller than are seen for reactions of most atomic transition metal ions with H₂ and D₂. Two, the peaks do not coincide with the bond dissociation energy of the neutral reactants $D^0(\text{H}_2) \approx D^0(\text{D}_2) \approx 4.5 \text{ eV}$.¹⁴ For most other metal ions, the cross sections peak fairly close to this energy since it is the thermodynamic onset for reaction (3):



The probability of this process increases with increasing collision energy and thus the cross section for forming stable MH⁺ (or MD⁺) decreases.

Also shown in Fig. 2 is the experimental excitation function for reaction (1) previously published by Halle, Armentrout, and Beauchamp (HAB).² The shapes and magnitudes of both sets of experimental data are similar and within experimental error. This is consistent with the fact that SI is used to produce Cr⁺ in both experiments.

As shown in Table I, Cr⁺ produced by SI is nearly pure ground state ⁶S. The possibility that an excited state of Cr⁺ is responsible for the reaction in Fig. 2 is exceedingly unlikely. If the first excited state, Cr⁺(⁶D), which comprises less than 0.2% of the SI beam were responsible for the observed reactivity, the true size of its reaction cross section would be unreasonably large (>50 Å²). To check this conclusion, Cr⁺ (produced by electron impact ionization of CrO₂Cl₂ at 42 eV, see below) was passed through a high pressure drift cell⁵ filled with methane.¹⁵ Collisions in this cell are expected to quench excited states.^{5,6} The reactivity of the Cr⁺ produced in this manner is identical with the results shown for Cr⁺(SI). Finally, studies of excited states of Cr⁺ (see below) further verify that the SI cross section is due primarily to Cr⁺(⁶S) with negligible contributions from Cr⁺(⁶D).

In past work, the threshold behavior of reactions like processes (1) and (2) have been modeled using simple em-

TABLE I. Low lying electronic states of Cr⁺.

State	Configuration	E(eV) ^a	Population ^b (%)
<i>a</i> ⁶ S	3 <i>d</i> ⁵	0.0	99.83 ± 0.06
<i>a</i> ⁶ D	4 <i>s</i> 3 <i>d</i> ⁴	1.52	0.17 ± 0.06
<i>a</i> ⁴ D	4 <i>s</i> 3 <i>d</i> ⁴	2.46	≤0.01
<i>a</i> ⁴ G	3 <i>d</i> ⁵	2.54	
<i>a</i> ⁴ P	3 <i>d</i> ⁵	2.71	
<i>b</i> ⁴ D	3 <i>d</i> ⁵	3.10	
<i>a</i> ² I	3 <i>d</i> ⁵	3.74	
<i>b</i> ⁴ P	4 <i>s</i> 3 <i>d</i> ⁴	3.78	

^aStatistical average of all *J* levels. Energies are taken from Ref. 8.

^bMaxwell-Boltzmann distribution at 2200 ± 100 K.

pirical models.^{2-6,16,17} More recently, we have found that phase space theory (PST) provides a remarkably accurate description of the shapes of the threshold regions of many endothermic ion-molecule reactions.^{3-6,18,19} Both empirical models and PST will be utilized here to analyze the threshold behavior of reactions (1) and (2).

In the case of the empirical fitting procedure, the general form for the energy dependence of endothermic reaction cross sections is given by Eq. (4):

$$\sigma(E) = \sigma_0(E - E_T)^n / E^m. \quad (4)$$

Here, E is the relative kinetic energy, E_T is the effective reaction threshold, σ_0 is a scaling factor, and n and m are variable parameters. The effective threshold is related to the true threshold E_0 for producing ground state products from ground state reactants by Eq. (5),

$$E_0 = E_T + E_{\text{rot}} + E_{\text{el}}, \quad (5)$$

where E_{rot} ($= 0.024$ eV) is the rotational energy of the H₂ (or D₂) reactant (vibrational energy is negligible) and E_{el} is the electronic energy of the Cr⁺ reactant ($= 0.0$ eV for the ⁶S state, Table I). Comparison to the data is made after convoluting over the experimental energy distributions as described above. More explicit treatments of the rotational states do not yield significantly different results.

In several previous studies,^{3,5,6,17} the successful models included the very simple line-of-centers (LOC) model given by $n = m = 1$. This is the most commonly used empirical model for interpreting reaction thresholds in metal ion-H₂ reactions.^{2,16} In this system, we confine our use of Eq. (4) to the LOC model. This is because the true reaction threshold is high, ≈ 3 eV, putting it in close proximity to the thermodynamic onset of reaction (3) at 4.5 eV. This can result in a true threshold behavior which does not resemble the experimentally observed cross section. Such behavior, documented for the reaction of Cu⁺ with H₂ where $E_0 = 3.56$ eV,⁶ makes the application of Eq. (4) unreliable when n and m are unconstrained. Consequently, we confine our analysis to the LOC model and only fit the data from threshold up to 3.5 eV. Below this energy, process (3) does not influence the shape of the reaction cross section.

The generality of the results of the LOC analysis are verified by comparison with results from a PST analysis. The PST calculations performed here use equations which are outlined elsewhere²⁰ and molecular constants which are listed in Table II. Calculations include explicit consideration of

all rotational states of H₂(D₂) populated at 305 K, the temperature of the gas cell. Vibrational states are populated to a negligible degree. Comparison with the data is made after convoluting the theoretical cross sections with the experimental energy distributions. Two parameters are allowed to vary in the PST calculations, the reaction endothermicity (E_0) and the overall magnitude, until the data is best reproduced as ascertained by a nonlinear least squares analysis.

For experiments where Cr⁺ is produced by SI, four independent H₂ and two D₂ data sets are analyzed. Both the LOC model and PST theory are found to describe the H₂ and D₂ data extremely well. The best LOC fit is shown as an example in Fig. 2. The average LOC E_0 is 3.12 ± 0.11 eV for the H₂ reaction and 3.20 ± 0.05 eV for the D₂ reaction. For the PST analysis, the data for reactions (1) and (2) are much smaller than the PST calculation ($\approx 4\%$). This is another indication that the reaction of Cr⁺(⁶S) with H₂ and D₂ is inefficient. The best PST threshold is 3.10 eV for both H₂ and D₂ data. The PST calculations are compared to averaged data sets for both H₂ and D₂ and this makes assigning an uncertainty difficult; however, changes in E_0 of 0.02 eV noticeably worsen the fit. The thresholds for reactions (1) and (2) should differ by the zero point energy, 0.046 eV higher for the D₂ reaction.²¹ This allows us to combine these results such that for reaction with H₂, the average E_0 is 3.11 ± 0.09 eV. This error is a conservative two standard deviation estimate which includes the absolute uncertainty in the energy scale (7 meV).

The fit shown in Fig. 2 includes a model for the high energy behavior which uses statistical assumptions within the constraints of angular momentum conservation to derive an expression for the probability of product dissociation.¹⁹ There are two parameters in this dissociation probability: E_D which is the energy at which dissociation begins and P which determines the steepness of the cross section decline. This model reproduces the cross sections for the direct reactions of Fe⁺(⁴F),^{5(b)} Co⁺(³F), Ni⁺(²D), and Cu⁺(¹S)⁶ with H₂ and D₂ over an extensive energy range (up to 9 eV) when E_D is set to its thermodynamic value and $p = 3$ is used. In our study of V⁺(⁵D) + H₂,³ this model also reproduced the reaction cross section with the correct value of E_D but required $p = 1$. This slower decline in the cross section at high energy indicates that more energy ends up in product translation. In order to reproduce the Cr⁺(SI) data, $p = 2$ is required as well as $E_D = 5.5$ eV, 1 eV above the thermodynamic value.

Cr⁺(EI) + H₂ and D₂

Figure 3 compares the results for reaction (2) where Cr⁺ has been produced by SI with the results for Cr⁺ produced by electron impact (EI) ionization of CrO₂Cl₂ and Cr(CO)₆. Similar EI results are obtained for reaction (1). The fact that these results differ from Cr⁺(SI) and vary with Ee demonstrates that they are phenomenological cross sections for a distribution of Cr⁺ electronic states. Results for ionization of CrO₂Cl₂ change little from Ee = 35 to 100 eV and those for Cr(CO)₆ are similar from Ee = 21 and 100 eV. At the highest values of Ee, the data in Fig. 3 show a small exothermic feature which is ≈ 0.002 times the collision

TABLE II. Molecular constants used in phase space calculations.

Diatomic	B_e^a (cm ⁻¹)	ω_e^a (cm ⁻¹)	$\omega_e x_e^{a,b}$ (cm ⁻¹)
H ₂	60.853	4401.2	121.34
D ₂	30.444	3115.5	61.82
CrH ⁺	6.66	1818	68.2
CrD ⁺	3.39	1298	34.7

^a Rotational and vibrational constants of diatom. Values for H₂ and D₂ are from Ref. 14. Values for CrH⁺ are from Ref. 23 and those for CrD⁺ are calculated from these.

^b Anharmonicity constant is calculated assuming a Morse oscillator potential well.

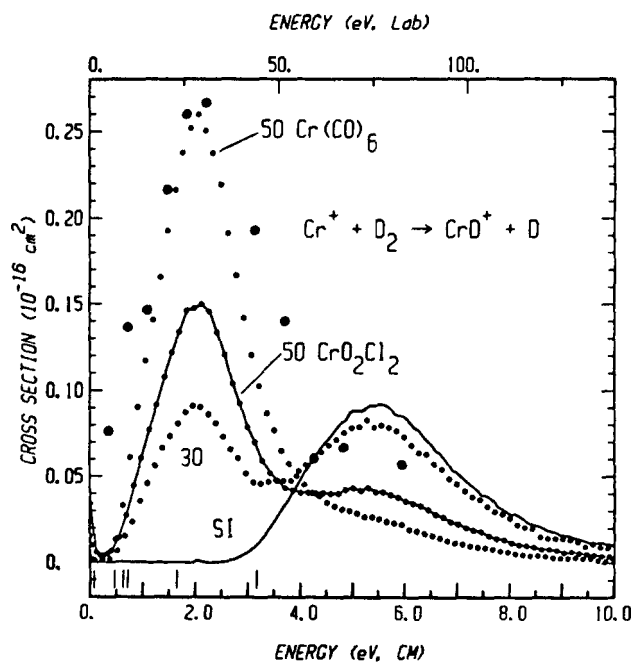


FIG. 3. Results for reaction of Cr^+ with D_2 as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Phenomenological cross sections are shown for distributions of Cr^+ states produced by surface ionization (SI, full line) and by electron impact (EI, small points) on CrO_2Cl_2 with a 30 and 50 eV electron energy and on $\text{Cr}(\text{CO})_6$ with a 50 eV electron energy. A full line runs through the 50 eV data points for EI on CrO_2Cl_2 for clarity. The large points show the data from Ref. 2 (reduced by a factor of 3) where Cr^+ is produced by EI on $\text{Cr}(\text{CO})_6$ with a 30 eV electron energy. Vertical lines indicate the expected thresholds E_T for the b^4D (0.03 eV), a^4P (0.42 eV), a^4G (0.59 eV), a^4D (0.67 eV), a^6D (1.61 eV), and a^6S (3.13 eV) states of Cr^+ .

cross section. This is presumably due to a very small amount of Cr^+ which has $E_{el} > 3.1$ eV, Table I. Two endothermic features are also apparent in the EI data. The magnitude of the high energy feature (which matches the behavior of the SI cross section) decreases with E_e . This is consistent with ground state Cr^+ (6S) being responsible for this feature. The low energy feature (which has an apparent threshold of 0.5 eV and a peak at ≈ 2 eV) has a magnitude which increases with E_e indicating that it is due to electronically excited Cr^+ . Clearly, these excited states are formed much more readily from $\text{Cr}(\text{CO})_6$ than from CrO_2Cl_2 . In addition, much less ground state Cr^+ is formed from the carbonyl. Part of this difference may be attributable to the fact that the appearance potential for forming Cr^+ from CrO_2Cl_2 is 19 eV¹⁰ and from $\text{Cr}(\text{CO})_6$ it is 15 eV.¹¹ However, even at high E_e , where the difference between these values is relatively minor, it is easier to produce excited Cr^+ from $\text{Cr}(\text{CO})_6$ than from CrO_2Cl_2 .

HAB reached similar conclusions concerning the production of excited states from a comparison of reaction (1) with Cr^+ produced by SI to that formed by EI on $\text{Cr}(\text{CO})_6$ at $E_e = 30$ eV.² The endothermic excited state feature reported by HAB is shown for comparison in Fig. 3. While HAB's cross section does have a shape similar to our data, its magnitude is ≈ 3 times greater than our data for $\text{Cr}(\text{CO})_6$. This is probably within the uncertainty of their absolute cross section measurement.

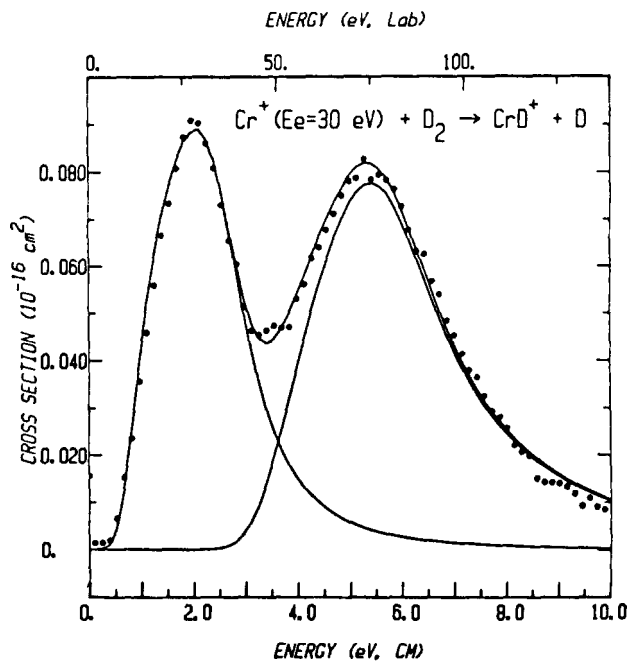


FIG. 4. Phenomenological cross sections for reaction of D_2 with Cr^+ produced by electron impact at a 30 eV electron energy as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). The data (points) are compared with a model (full lines) for the excited state behavior (peak at low energy), ground state behavior (peak at high energy), and their sum, see the text.

Using the reaction threshold established above for ground state Cr^+ (6S), we can analyze the low energy feature of the EI data to determine the identity of the electronically excited state or states. Using a LOC model, analysis of the reaction of D_2 with Cr^+ formed from CrO_2Cl_2 at several E_e 's yields an average value for E_T of 0.70 ± 0.10 eV. This fit is shown in Fig. 4. By using Eq. (5), we calculate that the reacting state(s) have $E_{el} = 2.43 \pm 0.14$ eV. This energy corresponds closely to excitation energy of the 4D state, Table I, but the 4G state is also a possibility. Clearly, one of these states is the primary reactant in the low energy region. When the low energy feature of the reaction of D_2 with Cr^+ formed from $\text{Cr}(\text{CO})_6$ at several E_e 's is analyzed, an average value for E_T of 0.67 ± 0.10 eV is obtained. This gives $E_{el} = 2.46 \pm 0.14$ eV. This indicates that EI on both CrO_2Cl_2 and $\text{Cr}(\text{CO})_6$ produces predominantly the same excited state(s). Only their population (relative to that of the ground state) changes appreciably. This is consistent with the analysis of HAB who used a different procedure to conclude that the electronic excitation in EI of $\text{Cr}(\text{CO})_6$ is 2.5 ± 0.3 eV.²

It is important to note that there is no obvious reaction having a threshold between that of Cr^+ (6S) at 3.1 eV and Cr^+ (4D)/ Cr^+ (4G) at 0.7 eV, Fig. 3. No such reaction is observed at any electron energy despite a very careful search for this effect (which included the use of the drift cell source, see above). This suggests that Cr^+ (6D) which has a thermodynamic threshold of 1.61 eV is either unreactive or is not formed appreciably by EI.

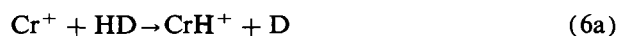
The fit shown in Fig. 4 also includes the model for the high energy behavior discussed above. Now, $p = 3$ and

$E_D = 2.35$ eV, slightly in excess of the thermodynamic value for Cr⁺(⁴D) of 2.07 eV. The fit shown in Fig. 4 is a sum of this model for the low energy feature and the excitation function of the SI data reduced by 19%. The fact that only these two contributions are required to reproduce the data is a further indication that reaction due to Cr⁺(⁶D) is not appreciable. Note also that this model indicates that excited states comprise $\approx 20\%$ of the $E_e = 30$ eV beam. Similar analyses of the $E_e = 50$ eV data for CrO₂Cl₂ and for Cr(CO)₆ indicate that excited states account for $\approx 40\%$ and $\approx 80\%$ of the Cr⁺ beam, respectively. This latter value agrees nicely with the results of Ridge and co-workers who determined that EI on Cr(CO)₆ where $E_e = 70$ eV, produces a 70.4% population of metastable excited Cr⁺.^{1(a)}

A comparison of PST calculations to the excited state cross sections is also illuminating. The PST results also reproduce the excited state behavior with the same threshold as the LOC analysis. The magnitude of the observed cross section at $E_e = 30$ eV is found to be $\approx 1.3\%$ of the PST calculation. This can be compared to the estimate of 20% excited state population obtained above. The discrepancy could be due to two effects. One, the excited states react at only ≈ 0.07 ($= 1.3/19$) of the PST prediction. Two, other excited states (such as the ⁶D) could be present up to 18% in the EI beam but are unreactive. Any combination of these effects is also conceivable. Similar analyses performed on the $E_e = 50$ eV CrO₂Cl₂ and Cr(CO)₆ data find that the excited state cross section is $6 \pm 2\%$ of the PST calculation after correcting for the approximate excited state population.

Cr⁺ + HD

An important tool used in the identification of the various reaction mechanisms listed in the introduction is the product branching ratios for the reactions with HD. Figure 5 shows the product excitation functions associated with reactions (6a) and (6b),



where Cr⁺ has been prepared by SI. The reaction threshold for both channels is comparable to that for reactions (1) and (2). Formation of CrD⁺ is favored over CrH⁺ by a factor of 2–3 in the threshold region. This is unusual behavior. Both the CrH⁺ and CrD⁺ cross sections peak near the dissociation energy of HD, 4.5 eV, but then there is a second feature in the CrH⁺ cross section. This has an apparent threshold at about 5 eV and peaks at ≈ 8 eV. This second feature is also unusual.

Although we find no evidence for participation of Cr⁺(⁶D) in the Cr⁺(SI) reactions with H₂ and D₂, we re-evaluate this conclusion here since the isotopic branching ratio in the HD reaction is often very sensitive to the presence of excited states. First, if Cr⁺(⁶D) were contributing to the SI reactions significantly, then its true cross section again would have to be unreasonably large. Second, by varying E_e from 20 eV, the approximate threshold for forming Cr⁺(⁶D) from CrO₂Cl₂, to 25 eV, we should be able to produce changes in the Cr⁺(⁶D) population which would be reflected in the observed cross section magnitudes. No such

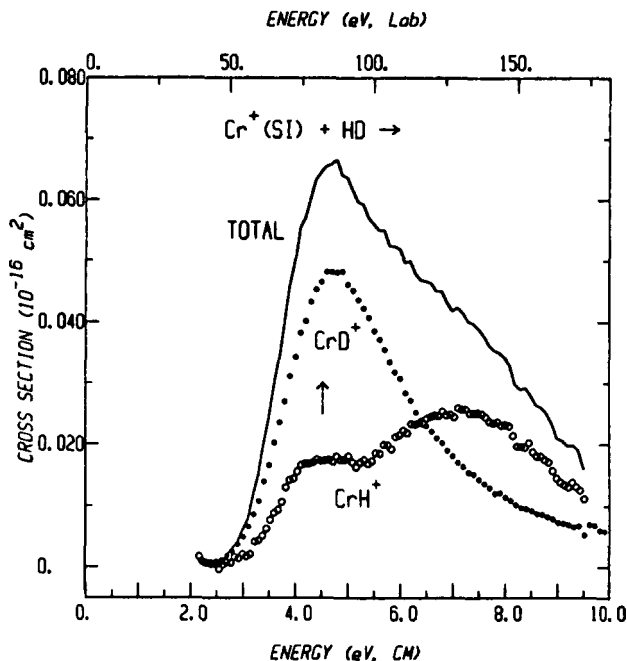


FIG. 5. Cross sections for reaction of HD with Cr⁺ produced by surface ionization (SI) as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Open and closed symbols show the results for production of CrH⁺ and CrD⁺, respectively. The line shows the total cross section. The arrow indicates the bond dissociation energy of HD at 4.52 eV.

changes are observed despite a careful examination. Finally, Cr⁺ produced by EI ionization of CrO₂Cl₂ at 42 eV and passed through a high pressure drift cell⁵ filled with methane (which is expected to quench excited states)^{5,6,15} is observed to react identically to Cr⁺(SI). We again conclude that the SI reaction cross sections are due predominantly to Cr⁺(⁶S) with negligible contributions from Cr⁺(⁶D). Thus the strange behavior of the HD reaction cross sections demonstrates that Cr⁺(⁶S) reacts by at least two energetically distinct mechanisms.

Figure 6 shows the product excitation functions for reactions (6a) and (6b), where Cr⁺ has been produced by EI on CrO₂Cl₂ with $E_e = 28$ eV. There are three endothermic features in the CrH⁺ channel which are now easily identified. The lowest energy feature has an apparent threshold near 0.5 eV, peaks at about 2 eV, and is undoubtedly due to the same excited states (⁴D and/or ⁴G) discussed above for the H₂ and D₂ reactions. The two higher energy features are associated with the ground state reaction shown in Fig. 5. The CrD⁺ channel has two endothermic features. The low energy feature is again due to reaction of electronically excited Cr⁺ while the high energy feature is due to ground state reaction.

Figure 7 shows the product excitation functions for reactions (6a) and (6b) where Cr⁺ has been produced by EI on CrO₂Cl₂ at $E_e = 50$ eV. As for reactions (1) and (2), the low energy features associated with excited Cr⁺ become larger with increasing E_e while the high energy features due to ground state Cr⁺ become smaller. Also, the small exothermic channel associated with highly excited Cr⁺ ($E_{el} > 3.1$ eV) is again present. It is now evident that the low energy

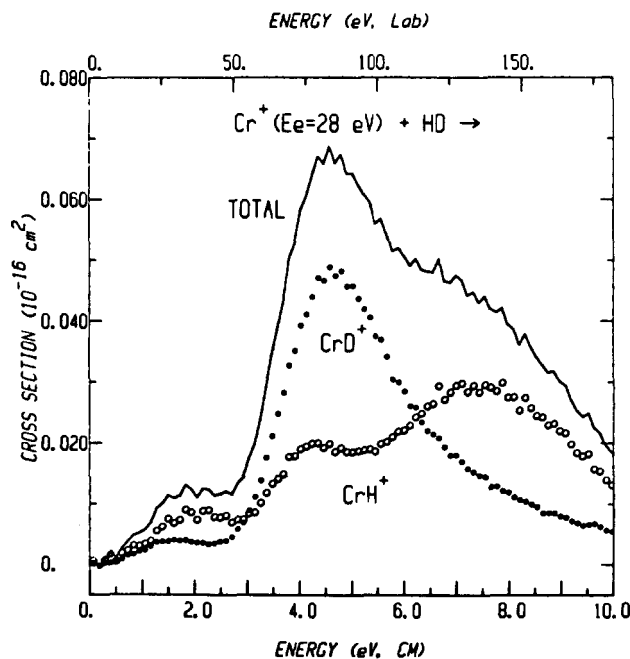


FIG. 6. Phenomenological cross sections for reaction of HD with Cr⁺ produced by electron impact at an electron energy of 28 eV as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Open and closed symbols show the results for production of CrH⁺ and CrD⁺, respectively. The line shows the total cross section.

reactivity favors production of CrH⁺, a result in contrast to the ground state reactivity. The ratio of cross sections for CrH⁺ to CrD⁺ shown in Fig. 6 varies from a factor of ≈ 1.5 near the 0.5 eV threshold up to a factor of ≈ 4 at 2.5 eV.

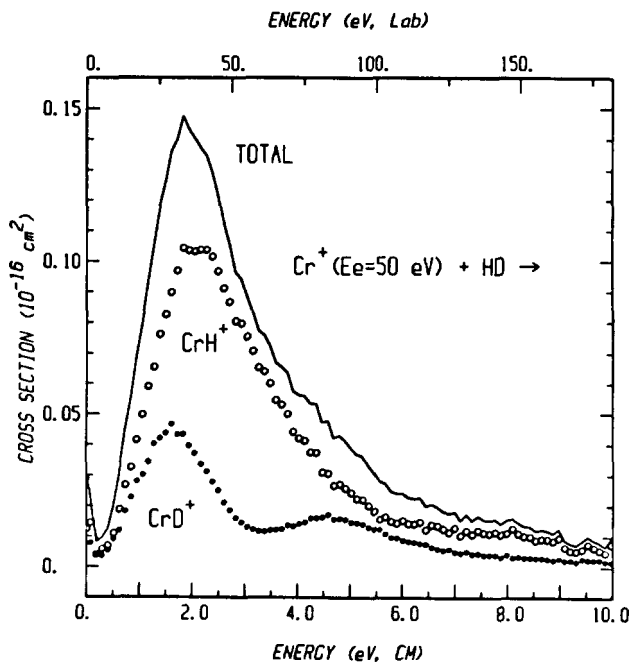


FIG. 7. Phenomenological cross sections for reaction of HD with Cr⁺ produced by electron impact at an electron energy of 50 eV as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Open and closed symbols show the results for production of CrH⁺ and CrD⁺, respectively. The line shows the total cross section.

DISCUSSION

Thermochemistry

The reaction threshold derived above, $E_0 = 3.11 \pm 0.09$ eV, can be related to the bond dissociation energy of CrH⁺ by Eq. (7) if we assume that no barrier to reaction in excess of the reaction endothermicity exists:

$$D_0^0(\text{CrH}^+) = D_0^0(\text{H}_2) - E_0. \quad (7)$$

This assumption is often quite accurate for ion-molecule reactions.²² Using $D_0^0(\text{H}_2) = 4.477$ eV,¹⁴ this yields a CrH⁺ bond energy at 0 K of 1.37 ± 0.09 eV (1.41 eV at 298 K). This value disagrees slightly with prepublication citations of our work, $D_0^0(\text{CrH}^+) = 1.20 \pm 0.09$ eV.^{23,24} This is primarily due to the more extensive threshold analysis performed here. The present value is in reasonable agreement with a 298 K value reported by HAB, 1.47 ± 0.17 eV,² who performed only a LOC analysis of reaction (1). *Ab initio* calculations yield 0 K bond energies of 1.05²³ and 0.98 eV,²⁵ about 0.35 eV lower than the value reported here. Typically, results of *ab initio* calculations are ≈ 0.13 eV lower than the experimentally determined values from this laboratory. The additional discrepancy for CrH⁺ may be due to the extensive electron correlation which must be properly accounted for in the CrH⁺ molecule (four nonbonding 3d electrons). A similar total discrepancy (≈ 0.34 eV) is seen for MnH⁺(⁶Σ),^{4,23} where the extent of electron correlation is similar (five nonbonding 3d electrons).

The CrH⁺ bond energy measured here fits in nicely with those for other diatomic transition metal hydride ions.²⁴ Analyses of the periodic trends in these bond energies has shown that they vary with the energy required to promote from the ground electronic state of the metal ion to a $4s3d^{n-1}$ configuration where the 4s electron is spin decoupled from the 3d manifold.^{23,24} Indeed, the value derived here for $D_0^0(\text{CrH}^+)$ makes this correlation much better.

Ground state reactivity

While Cr⁺(⁶S) has a $3d^5$ configuration, it does not react as a group #2 ion. Evidence supporting this conclusion is quite extensive. First, the absolute magnitude of the cross section for reaction (1) is small, reaching a peak of only 0.11 \AA^2 . This is much smaller than the maximum cross sections observed for other group #2 ions: Fe⁺(⁴F, $3d^7$) – 2.2 \AA^2 , Co⁺(³F, $3d^8$) – 1.8 \AA^2 , Ni⁺(²D, $3d^9$) – 1.4 \AA^2 , and Cu⁺(¹S, $3d^{10}$) – 0.8 \AA^2 . Since Cr⁺(⁶S) has a reaction threshold ($E_0 = 3.11$ eV) between that of Ni⁺ ($E_0 = 2.80$ eV) and Cu⁺ ($E_0 = 3.56$ eV), we would have expected a maximum cross section of $\approx 1.1 \text{ \AA}^2$. Another measure of the efficiency of the reaction is to compare with the absolute cross section predicted by phase space theory (PST). The group #2 ions mentioned above typically react with H₂ at 50%–100% of the PST calculation while Cr⁺(⁶S) reacts at $\approx 4\%$ of the PST prediction. Second, reaction of Cr⁺(⁶S) reaches its maximum cross section at about 5.5 eV. The other group #2 ions reach maxima very close to the thermodynamic limit for the onset of process (3), product dissocia-

tion. This behavior is quantified by the model for the high energy dependence in the cross sections. For Fe⁺ (⁴F), Co⁺ (³F), Ni⁺ (²D), and Cu⁺ (¹S), the onset of dissociation comes precisely at the thermodynamic limit. For Cr⁺ (⁶S), it is delayed by about 1 eV. Third, Cr⁺ (⁶S) reacts differently with HD than group #2 ions. These favor MH⁺ at all energies and do not exhibit the bimodal behavior evident in Fig. 5. Neither is this behavior like group #1 ions which react efficiently, peak at the thermodynamic limit, and produce equal amounts of MH⁺ and MD⁺ in reaction with HD.

The type of behavior exhibited by Cr⁺ (⁶S) is most similar to reactions of group #4 ions having high-spin 4s3dⁿ⁻¹ electron configurations. This has been documented for Mn⁺ (⁷S, 4s3d⁵)⁴ and Fe⁺ (⁶D, 4s3d⁶)⁵ and also appears to be consistent with the behavior of Ni⁺ (⁴F, 4s3d⁸).⁶ First, Mn⁺ (⁷S) and Fe⁺ (⁶D) clearly react inefficiently. They have cross section maxima of 0.09 and 0.15 Å², respectively, despite the fact that their thermodynamic thresholds (*E*₀ = 2.47 and 2.33 eV, respectively) are similar to that of Co⁺ (³F). Compared to PST calculations, the reaction efficiencies at threshold are 0.11% and 1.2%, respectively. Second, these ions reach their maximum cross section at high energies: ≈8.5 eV for Mn⁺ (⁷S) and ≈7 eV for Fe⁺ (⁶D). Third, these ions react with HD to produce the metal deutride ion as the major product although the bimodal behavior of the CrH⁺ species is not evident for these metal ions.

The reactivity of the group #4 ions has been described^{4,5} in terms of two distinct reaction mechanisms: an inefficient reaction beginning at the thermodynamic threshold and an impulsive reaction which has an onset and maximum above the thermodynamic limits. In the case of Cr⁺ (⁶S), this type of behavior is most clear in the HD cross sections, where the first feature of the CrH⁺ channel is due to thermodynamic behavior and the second feature is due to impulsive behavior. Indeed, the dual character of the reaction mechanism is not exhibited this clearly in the Mn⁺ and Fe⁺ systems. Why then do the CrD⁺ channel from HD and the H₂ and D₂ cross sections not exhibit two features? According to a simple pairwise model for impulsive behavior (described in detail elsewhere),⁴ the peak in the CrD⁺ channel should occur at half the energy of the peak in the CrH⁺ channel, or about 4 eV. For H₂ and D₂, the model predicts that the peaks should occur at two-thirds this energy or about 5 eV. Thus we believe the impulsive behavior in these reaction channels merges with the thermodynamic behavior and is not clearly observed. This is also the case for the reactions of Mn⁺ and Fe⁺ with H₂ and D₂.

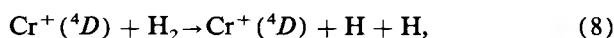
While the relative positions of the cross section peaks for Cr⁺ + H₂, HD, and D₂ is predicted qualitatively by the pairwise model, there is not quantitative agreement. A similar but less severe deviation from the pairwise model is observed in the Fe⁺ (⁶D) system. The Mn⁺ (⁷S) system comes closest to exhibiting strict pairwise behavior. These deviations from exact pairwise behavior are paralleled by the extent of thermodynamic behavior exhibited by these systems. Mn⁺ (⁷S) shows the least (0.1%); Fe⁺ (⁶D) somewhat more (1.2%); and Cr⁺ (⁶S) still more (4%). We believe this is a reflection of how repulsive the potential energy surface is. This is discussed further below.

Excited state reactivity

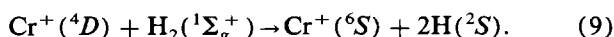
Cr⁺ (⁶D) has a high-spin 4s3d⁴ configuration (group #4 ion) and therefore is expected to have a very small reaction cross section. This is consistent with the fact that we see no evidence for reaction by this state. While it is possible that this is because none of this state is formed by EI, there is circumstantial evidence which suggests that it is. More direct evidence concerning the reactivity of the ⁶D state will require methods which allow it to be produced selectively so that it can be studied in the absence of the reactions of other states.

Analysis of the low energy feature in the EI data reveals that either the ⁴D or the ⁴G state is probably responsible for reaction there. Note that this conclusion clearly implies that the same state of CrH⁺ is formed by reaction of the Cr⁺ excited state and by reaction of Cr⁺ (⁶S). This is a perfectly reasonable possibility which is discussed further below. The excited state(s) react with HD to form CrH⁺ preferentially. We have previously interpreted this isotope ratio to indicate a direct reaction.^{3,5,6} This result is consistent with what we expect from the ⁴D state which has a low-spin 4s3d⁴ configuration (group #3). In contrast, group #1 ions [such as the ⁴G(3d⁵)] are observed to form nearly equal amounts of CrH⁺ and CrD⁺ in reaction with HD.³ We are therefore inclined to identify the ⁴D state as the primary excited state reactant in the EI beam from both CrO₂Cl₂ and Cr(CO)₆. This conclusion is consistent with the general observation that the most prominent states produced by EI are typically the lowest members of a particular spin manifold.³⁻⁶ In the case of Cr⁺, these are the ⁶S and ⁴D states.

While the cross section for a ground state atomic ion reacting with H₂ typically peaks near the threshold for process 3, 4.5 eV, the reaction of an electronically excited atomic ion can be more complex. If, for example, Cr⁺ (⁴D) remains in its original electronic state as in process (8):



the reaction cross section should again peak at *D*⁰(H₂) ≈ 4.5 eV. In past work,^{3,4} we have seen no evidence for process (8). Instead, the cross sections for the reactions of electronically excited V⁺,³ Mn⁺,⁴ and Ti⁺²⁶ with H₂ tend to peak near *D*⁰(H₂) - *E*_{el} - *E*_{rot}. This corresponds to a quenching process such as reaction (9):²⁷



The fact that both reactions (8) and (9) can occur for Cr⁺ (⁴D) may help explain why the dissociation energy (*E*_D) used to model the behavior of the excited state cross section is higher than the thermodynamic value. Since the observed deviation is fairly small (≈0.3 eV), the excited state reacts at higher energies primarily by reaction (9) but a small contribution from process (8) also may be present. Another possible explanation of this deviation may be the presence of a small amount of reaction by the ⁶D state.

Potential energy surfaces

In order to better understand the behavior observed in the reaction of Cr⁺ with hydrogen, it is appropriate to consider the gross features of the potential energy surfaces. As

Cr⁺ (⁶S, 3d⁵) and H₂ (¹Σ_g⁺) approach each other, a single sextet surface evolves. Diabatically (i.e., referring to a single electron configuration), this surface leads to the formation of a 3dσ–1s bonded CrH⁺ (⁵Σ) + H(²S). As Cr⁺ (⁶D) and H₂ approach each other, there are five sextet surfaces which diabatically correlate with H(²S) + CrH⁺ (⁵Σ, ⁵Π, ⁵Δ). These states have a 4s–1s M⁺–H bond. Adiabatically, the two ⁵Σ states (and also the sextet surfaces evolving from these states) mix such that there is an adiabatic surface leading from group state reactants, Cr⁺ (⁶S) + H₂, to ground state products, CrH⁺ (⁵Σ) + H(²S), see the Appendix. Adiabatically, the Cr⁺ (⁶D) + H₂ reactants lead only to the excited CrH⁺ (⁵Σ, ⁵Π, and ⁵Δ) product states. This qualitative picture is consistent with the observation that Cr⁺ (⁶S) can react at the thermodynamic threshold to form ground state CrH⁺. It also may help explain why the Cr⁺ (⁶D) state is unreactive.

An analogous treatment can be performed for the Cr⁺ quartet states. As Cr⁺ (⁴D, 4s3d⁴) and H₂ approach each other, there are five quartet surfaces which diabatically correlate with the 4s–1s bonded CrH⁺ (⁵Σ, ⁵Π, and ⁵Δ). More highly excited quartet states of Cr⁺ with 3d⁵ configurations diabatically correlate to the 3dσ–1s bonded CrH⁺ (⁵Σ) and higher lying excited states. As in the case of the sextet surfaces, the 3d⁵ states and 4s3d⁴ states should mix such that Cr⁺ (⁴D) diabatically correlates with ground state CrH⁺ (⁵Σ). The higher lying quartet states diabatically correlate to excited product states. It is now clear why the reactive excited states of Cr⁺ are observed to form the same product state as Cr⁺ (⁶S). These ideas also further support the identification of the ⁴D state as the primary reactant.

We now seek to explain why Cr⁺ (⁶S) reacts inefficiently despite its adiabatic correlation with the ground state of CrH⁺. A convenient way to consider this is to look at the reaction in reverse. As H(²S) approaches CrH⁺ (⁵Σ), both quartet and sextet surfaces are formed. In order to produce H₂ (¹Σ_g⁺) and Cr⁺ (⁶S), the 1s electron on the hydrogen atom must be high-spin coupled to the nonbonding 3d electrons on the metal. In a collinear Cr⁺–H–H geometry, this secondary interaction is not important, but in off-collinear geometries, this leads to a repulsive interaction between the metal and the incoming H atom. We have used identical arguments to explain the inertness of metal ions with high-spin 4s3d^{n–1} configurations, e.g., Mn⁺ (⁷S)⁴ and Fe⁺ (⁶D).⁵ Indeed, the fact that Mn⁺ (⁷S) is much less reactive than Fe⁺ (⁶D) or Cr⁺ (⁶S) is presumably because it has five nonbonding 3d electrons while the others have only four. In contrast, in order to produce H₂ (¹Σ_g⁺) + Cr⁺ (⁴D), the H atom must be low-spin coupled with the nonbonding 3d electrons on the metal. This leads to attractive bonding interactions in all geometries. Naturally, these same considerations hold for reaction in the forward direction.

These considerations also explain why Cr⁺ (⁶S, 3d⁵) reacts differently than group #2 ions. The potential energy surface (PES) evolving from Cr⁺ (⁶S) must interact strongly with that from Cr⁺ (⁶D) in order to form ground state CrH⁺ (⁵Σ), see the Appendix. This leads to the rather restricted reaction geometry characteristic of the group #4 ions. In contrast, metal ions with 3dⁿ (n > 5) configurations

have the same spin as a low-spin coupled 4s3d^{n–1} configuration. Therefore, the PES's for group #2 ions must interact strongly with those evolving from group #3 ions in order to form ground state MH⁺. Thus, the 3d⁵ configuration is unique because it must occupy the 3dσ orbital excluding it from group #1 and it has the wrong spin to be in group #2. No other metal ion configuration falls between the cracks of our initial categorization the way that Cr⁺ (⁶S) does.

This report provides strong, new evidence in support of our description of the relationship between the electronic structure of the reactant and the mechanism by which it can interact with hydrogen. The prominent factors are: (1) occupation of the 4s or 3dσ orbitals inhibits insertion; (2) if either of these orbitals are occupied, reaction can occur via a direct mechanism if the metal ion is in a low spin state (i.e., having the same spin as ground state MH₂⁺); and (3) if the 4s or 3dσ is occupied and the metal ion is in a high-spin state, reaction is sterically hindered such that it is inefficient at threshold and largely impulsive. Since these reactivity guidelines refer to particular electron configurations, they are "diabatic" in nature. The present study makes it clear that the interactions of these diabatic potential energy surfaces (to form adiabatic reaction surfaces) are very important to a detailed understanding of the reactions of transition metal ions. Additional evidence for these types of considerations continue to be studied in our laboratory and have now been observed in a number of systems.

ACKNOWLEDGMENT

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APPENDIX

A qualitative picture of the low lying states of CrH⁺ can be obtained by using atomic coupling arguments. This method has been described in detail for the application to neutral transition metal hydrides²⁸ and also has been applied to several cases of transition metal hydride ions.^{3–6} We begin by presuming that a metal–hydrogen bond is formed between the metal 4s and the H 1s orbital (as suggested by a periodic trends analysis).^{23,24} The remaining four electrons can then be placed in the nonbonding metal 3d orbitals. The energies of the different 3d orbital occupancies can then be ascertained from the energies of the corresponding atomic states. The five different 3d orbital occupancies are all pure ⁵D, Table III. In the case of Cr⁺, the 4s electron must be includ-

TABLE III. States of CrH⁺.

Molec configuration				Atomic state	Molecular state	Relative energy (eV)
3dδ	3dπ	3dσ	4s–1s	3d ⁴ (⁵ D)4s		
1	2	1	2	1.0	⁵ Δ	1.99
2	1	1	2	1.0	⁵ Π	1.99
2	2	0	2	1.0	⁵ Σ	1.99
3dδ	3dπ	3dσ–1s		3d ⁵		
2	2	2		1.0	⁵ Σ	1.10

ed. The energy of these $4s3d^4$ configurations are given by spin decoupling the $4s$ from the $3d$ electrons. Thus, the $3d^4(^5D)4s$ energy of 1.99 eV comes from an average of the $a^6D[3d^4(a^5D)4s]$ state at 1.52 eV, Table I, and the $a^4D[3d^4(a^5D)4s]$ state at 2.46 eV. From this atomic information, it is unclear whether the $^5\Sigma$, $^5\Pi$, or $^5\Delta$ will be the ground state of CrH⁺.

To make this differentiation, we must consider binding the hydrogen atom to Cr⁺ in a $3d^5$ configuration. Now, the bonding orbital on the metal is the $3d\sigma$ and as shown in Table III only a $^5\Sigma$ state of CrH⁺ is possible. Calculating the energy of this $3d\sigma-1s$ bound state requires decoupling the spin of the $3d\sigma$ orbital from the other $3d$ electrons. The high-spin components of this configuration all come from the 6S state of Cr⁺ with an energy $E(^6S) = 0$ eV. The low-spin components are mixtures of the 6S , 4D , and 4G states. The analysis required is outlined elsewhere^{16(b)} and is substantially more complicated than that for the $3d^44s$ case. The result is that the energy of the low-spin component of the $3d^5$ atomic configuration is $E(^6S)/5 + 18E(^4G)/35 + 2E(^4D)/7 = 2.20$ eV. Thus the energy for the spin decoupled atomic state, 1.10 eV, is the average of this energy and that of the 6S high-spin component.

These atomic state energy level considerations suggest that the $3d\sigma-1s$ bonded CrH⁺ ($^5\Sigma$) is a lower energy molecule than the $4s-1s$ bound CrH⁺ ($^5\Sigma$). However, the $4s-1s$ bond is inherently stronger than the $3d\sigma-1s$ bond. This is evident from an analysis of the periodic trends in first row transition metal hydride ion bond energy,^{23,24} which shows that the bond energies correlate extremely well with the energy required to promote the reactant metal ion to a spin decoupled $4s3d^{n-1}$ configuration. This effect is likely to bring the two diabatic $^5\Sigma$ states much closer in energy. They can then mix such that one of the $^5\Sigma$ states will decrease in energy and the other will increase. The final prediction is that the ground state of CrH⁺ is $^5\Sigma$. Further, the bonding can be expected to have substantial amounts of both $4s$ and $3d$ metal character. These qualitative arguments are guided by *ab initio* calculations²³ which obtain a $^5\Sigma$ ground state with a Cr-H⁺ bond that is 47% $3d\sigma$ character, 40% $4s$ character, and 13% $4p$ character.

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