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ELECTRONIC STATES OF CHROMIUM CARBENE IONS CHARACTERIZED BY HIGH-RESOLUTION TRANSLATIONAL ENERGY LOSS SPECTROSCOPY

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The electronic states of the unsaturated organometallic carbene $CrCH_2^+$ are investigated using high-resolution translational energy loss spectroscopy. The observed energy loss feature (1.05 ± 0.2 eV) is in good agreement with theoretical calculations which predict two higher lying states, $^6B_1$ and $^6A_1$ at 0.78 and 0.82 eV respectively, above the $^4B_1$ ground state of $CrCH_2^+$.

1. Introduction

Rapid progress in experimental methodology has made it possible to generate and study highly reactive organometallic fragments in the gas phase. While experimental investigations have focused mainly on the reactivity and thermochemical stability of such species [1–7], parallel developments in ab initio theory have provided descriptions of the molecular and electronic structures of these molecules [8–10]. Transition metal carbenes, species which contain a divalent carbon bonded to a transition metal center, are an example of reactive organometallic fragments which have been the subject of both experimental and theoretical investigations.

Ion beam [1–3] and ion cyclotron resonance [4–7] techniques have recently been used to investigate the energetics and reactions of both the coordinately saturated and "bare" transition metal carbenes. In the latter category it has been observed [1,4] that the chromium carbene ion, $CrCH_2^+$, can be generated by reaction of electronically excited Cr^+ with methane:

$$Cr^+ + CH_4 \rightarrow CrCH_2^+ + H_2 . \tag{1}$$
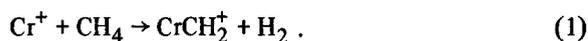
Reaction (1) is 45 kcal/mol *endothermic* for ground-state Cr^+ (^6S derived from the d^5 configuration) [11], but is 12.5 kcal/mol *exothermic* if the Cr^+ ion is in the ^4D excited state. Several experimental results [1,4] suggest that it is, in fact, the ^4D state (derived from the s^1d^4 configuration and 2.5 eV higher in energy than the ground state) [11] which is responsible for the production of $CrCH_2^+$ by reaction (1).

Recent ab initio calculations of the low-lying electronic states of $CrCH_2^+$ by Carter and Goddard [8] predict that the ground state of $CrCH_2^+$ is a $^4B_1$ state, with a directly calculated bond dissociation energy $D_e = 44$ kcal/mol and an estimated exact bond dissociation energy of $D_{corr} = 50$ kcal/mol. This can be compared with the experimentally determined [1] bond energy of 65 ± 7 kcal/mol. Earlier CI calculations by other workers [9] suggested that the $CrCH_2^+$ ground state is the $^6B_1$ state, with a significantly weaker bond, while Carter and Goddard [8] found the $^6B_1$ state to be 18 kcal/mol higher in energy than the $^4B_1$ state. In an attempt to resolve the situation, we have employed high-resolution translational energy loss spectroscopy to investigate the electronic states of $CrCH_2^+$.

2. Experimental

The theory and instrumentation for translational energy loss spectroscopy have appeared in detail elsewhere [12,13] and will be described only briefly. Experiments were performed at UCSB using a double focusing mass spectrometer (VG ZAB-2F). A variable temperature ion source was operated at 330 K with 6.5×10^{-3} Torr total pressure. Chromium ions are formed from 150 eV electron impact ionization of $Cr(CO)_6$. Reaction of excited-state Cr^+ with CH_4 (reaction (1)) produces $CrCH_2^+$. Ions extracted from the source are accelerated to 8 kV, mass selected by a magnetic sector and focused into a collision cell. Typically, 10^{-3} Torr of helium is used as the collision gas. Translational energy analysis of the unscattered main ion beam and its scattered components is accomplished with an electrostatic analyzer, located after the collision chamber and collinear with the incident ion beam axis. In the absence of a collision gas, the energy resolution of the main beam (Cr^+ or $CrCH_2^+$) was 0.2 eV (fwhm).

During the collision between a neutral target and an ion, which has been accelerated to several kilovolts, the internal energy of the ion may be altered in this situation, peaks at higher and/or lower energies than the unscattered ion beam (corresponding to de-excitation and excitation, respectively, of ionic states) are observed. The reported experiments are sensitive to collisions occurring at small scattering angles, for which translational energy losses of the ion correspond to changes in the ion internal energy [13]. Ions with the same nominal mass as the ion of interest may also appear in the spectrum but are easily identified with the high-resolution capabilities of the instrument. In the case of chromium carbene ($^{52}CrCH_2^+$), other ions of mass 66 were also observed in the high-resolution energy loss spectrum but did not occur in a region which would obscure the predicted electronic transitions.

3. Results and discussion

Although collisional excitation can generate states that are difficult to prepare by optical methods, processes which are optically "allowed" are generally observed to have a larger cross section for collisional excitation than those which are optically "forbidden"
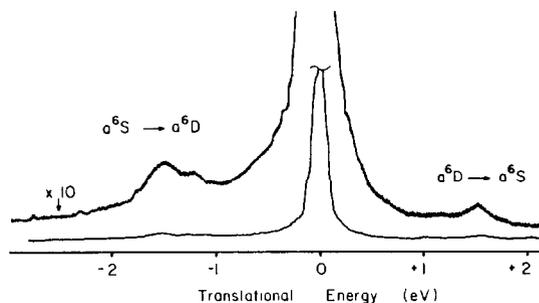

Fig. 1. Translational energy loss spectrum of Cr^+ scattered from helium ($P_{He} = 6 \times 10^{-3}$ Torr).

[12]. For transition metal systems, it is not uncommon to have numerous electronic states of the same or different spin multiplicity close in energy to the ground state. In order to determine the relative magnitudes of the collisional excitation cross sections for transition metal ions, the high-resolution translational energy loss spectrum of Cr^+ scattered from He was investigated (fig. 1). The main peak at zero translational energy loss in fig. 1 corresponds to the unscattered Cr^+ beam. Two smaller features occur 1.45 eV lower and higher in energy than the main beam. As shown in table 1, this energy change corresponds to the spin allowed $a\,^6S \rightarrow a\,^6D$ excitation and $a\,^6D \rightarrow a\,^6S$ de-excitation, respectively. Also from table 1, one can see that this is the only transition involving the ^6S ground state which would occur below 2 eV. Transitions between the quartet states of Cr^+, specifically the $a\,^4D \rightarrow b\,^4P$ and the $a\,^4G \rightarrow b\,^4P$, would appear at 1.17 and 1.23 eV, respectively, and may in fact be present but obscured by the $^6S \rightarrow\,^6D$ transition. Transitions between the $a\,^4D$ and $a\,^6S$ states at

Table 1
Low-lying electronic states of chromium ion

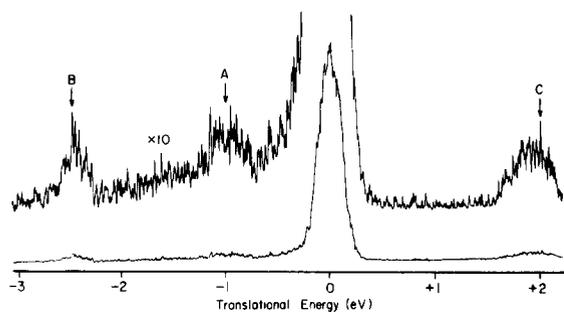| State	Configuration	Energy (eV) [a]
$a\,^6S$	$3d^5$	0.00
$a\,^6D$	$3d^4s^1$	1.48
$a\,^4D$	$3d^4s^1$	2.42
$a\,^4G$	$3d^5$	2.54
$a\,^4P$	$3d^5$	2.71
$b\,^4D$	$3d^5$	3.10
$b\,^4P$	$3d^4s^1$	3.71
$a\,^2P$	$3d^5$	3.74

[a] Data taken from ref. [11] refer to lowest J state.

Fig. 2. Translational energy loss spectrum of $^{52}CrCH_2^+$ scattered from helium (P_{He} = 6 X 10^{-3} Torr). The feature marked "A" is from $^{52}CrCH_2^+$, while "B" and "C" are from mass impurities.

Table 2
Low-lying electronic states of $CrCH_2^+$ ion

State	Configuration	Energy (eV)
$^4B_1$	$Cr^+(^6S)$ + $^3B_1$ CH_2	0.00
$^6B_1$	$Cr^+(^6S)$ + $^3B_1$ CH_2	0.78
$^6A_1$	$Cr^+(^6S)$ + $^1A_1$ CH_2	0.82

2.42 eV were not observed. The apparent collisional cross section for these excitation processes is small. This could be due to either a small value of the transition matrix elements linking these states, a small population of the initial states, or both [12,13].

The translational energy loss spectrum for $CrCH_2^+$ scattered from He is displayed in fig. 2. An excitation peak labeled "A" appears 1.05 eV lower in energy than the main beam. No superelastic (higher-energy)

peaks or metastable transitions are observed. The other two peaks indicated in fig. 2 ("B" and "C") result from $^{54}CrC^+$ and $^{50}CrCH_4^+$, which have the same nominal mass as $^{52}CrCH_2^+$, but which otherwise have no bearing on the present study.

The recent ab initio calculations of Carter and Goddard [8] for the electronic states of $CrCH_2^+$ can be used to assign the transitions observed in the translational energy loss spectrum of $CrCH_2^+$. The authors predict a $^4B_1$ ground state, which is best envisioned as a high-spin ^6S Cr^+ forming a *covalent* double bond with a $^3B_1$ CH_2 fragment. Two low-lying excited states were calculated: a $^6B_1$ state, consisting of a single covalent σ bond between ground-state (^6S) Cr^+ and CH_2, with the Cr^+ and CH_2 π electrons high-spin
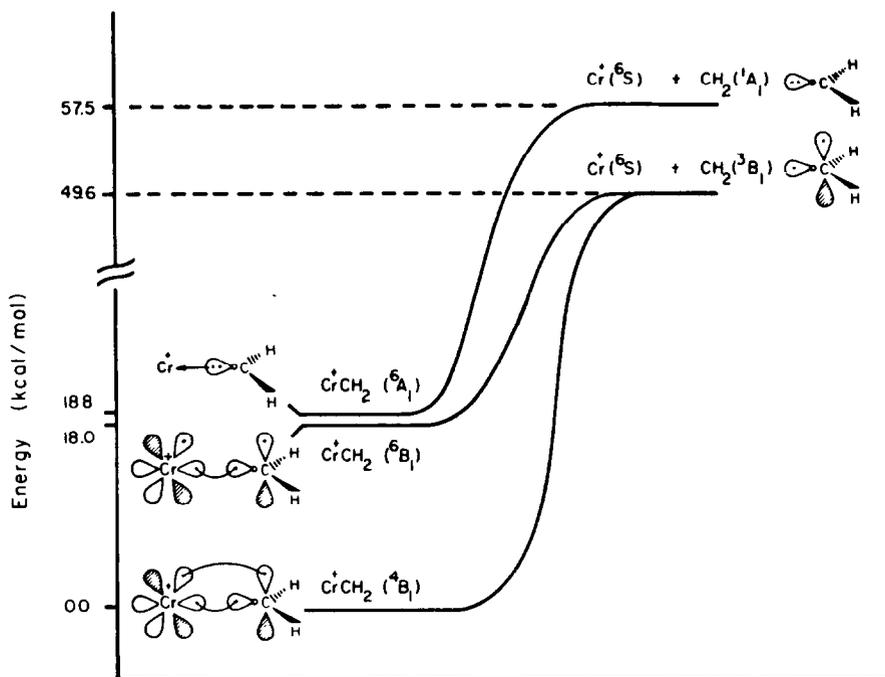

Fig. 3. Adiabatic electronic state correlation diagram for low-lying states of $^{52}CrCH_2^+$. Data from refs. [8,14].

coupled to the other valence d electrons, lies 18.0 kcal/mol (0.78 eV) above the $^4B_1$ ground state, and the $^6A_1$ state [14], composed of a single σ donor bond between the ground-state (^6S) Cr^+ and excited-state ($^1A_1$) CH_2, calculated to lie 18.8 kcal/mol (0.82 eV) above the $^4B_1$ ground state of $CrCH_2^+$. These results are summarized in table 2 and shown with schematical descriptions of the bonding orbitals in fig. 3.

The experimentally observed translational energy loss feature at 24.2 kcal/mol (1.05 ± 0.2 eV) obtained in this investigation is in good agreement with the theoretical predictions for electronic excitation of the $^4B_1$ ground state to either $^6B_1$ or $^6A_1$ states of $CrCH_2^+$. The calculations of Carter and Goddard [8] indicate that vibrational excitation (0.4 eV for the C—H stretch of the $^4B_1$ ground state and $^6B_1$ excited state) could also be resolved with this technique. There is no evidence for vibrational excitation of either the ground or excited state at this S/N ratio. In contrast to the translational energy loss spectrum of Cr^+ ions, where only spin allowed transitions are readily apparent, the $CrCH_2^+$ excitations are attributed to spin forbidden transitions, and the small cross section inferred from the weak signal is consistent with this assignment.

Unsaturated metal species such as $CrCH_2^+$ are of interest as prototypes for organometallic species implicated in numerous catalytic reactions. This study suggests that high-resolution translational energy loss spectroscopy can be successfully applied to investigations of the excited electronic states of a wide range of reactive organometallic species which can be formed in the gas phase. It is also encouraging that, in this case, the agreement between the experimental determination and the theoretical predictions is quite good.

Acknowledgement

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