# Infrared Multiphoton Chemistry of Transition Metal/Ethanol Ion Complexes

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**Abstract:** A detailed study has been undertaken of the infrared multiphoton chemistry of complexes of the general form $M^+(C_2H_5OH)_n$, where M is chromium, manganese, iron, cobalt, or nickel and *n* is either 1 or 2. The ions have been prepared via ligand stripping from volatile metal−carbonyl compounds and held in an ion trap, where photofragment intensities have been recorded as a function of $CO_2$ laser frequency by using radiation from a line-tuneable laser. All the metal complexes exhibit structured photofragmentation patterns as a function of laser frequency, and the results are consistent with the absorber being an adduct of $M^+$ bonded to ethanol via ion−dipole and −induced dipole interactions. For the metals Fe, Ni, and Co, photoexcitation of the complex promotes a dehydration reaction, whereas for Mn and Cr, the metal ion−ethanol bond is broken upon photoexcitation. In association with iron, the efficiency of the photoexcitation process is very dependent upon isotopic substitution, and the relative intensities of $H_2O$, DHO, and $D_2O$ from complexes composed of mixtures of isotopomers show evidence of both primary and secondary isotope effects. Overall, the results show a strong correlation between the reaction pathway of an ion complex and the electronic spin configuration of the metal ions concerned. Those metal ions that are in low spin states with no 4s electrons are found to exhibit the dehydration reaction.

## I. Introduction

The research field of transition metal ion chemistry has been active for almost two decades, having been initiated by Allison and Ridge in two important papers which covered gas-phase reactions with alcohols and alkyl halides.[1,2] In the intervening period the topic has undergone a remarkable expansion with many examples being identified of reactions where specificity is governed by thermodynamics, valence electron configuration, or spin state of the metal.[3−6] In many instances, the actions of metal ions have been identified as being very selective in terms of bond activation and reaction pathway.

The gas-phase chemistry of the iron cation has been the subject of particular attention. The early experiments of Allison and Ridge[1,2] investigated the reactions of $Fe^+$ with ethanol, for which they proposed an initial metal atom insertion step followed by $\beta$-hydrogen transfer and leading finally to dehydration. Subsequent work by Schwarz and co-workers[3,7,8] examined the reactions of $Fe^+$ with a broad range of alcohols and related molecules. Alternatives to dehydration, such as dehydrogenation, were identified in long-chain alcohols and characterized in terms of cyclic transition states. In addition, the concept of remote functionalization has been introduced as an alternative to metal ion insertion, to account for cetain reaction pathways in long-chain alcohols.[9]

In many of the recent studies of metal ion chemistry the source of activation has been collisional energy, either during complex formation or immediately following mass isolation. As an alternative, we present here results from a series of experiments where a low-powered (<50 W), line-tuneable $CO_2$ laser has been used as the source of excitation. The effect of the laser is to promote chemical processes within transition metal ion/ethanol complexes via multiphoton infrared excitation, and individual complexes have been prepared and held in an ion trap, where they have been subjected to laser irradiation. In addition to providing evidence of photoinduced dehydration the experiments also exhibit a dependence on laser frequency. From the frequency-dependent photofragmentation patterns, it is possible to discuss the nature of the chromophore in terms of the vibrational mode(s) responsible and to comment on the structure of the complex. The advantages of low-powered infrared excitation are that it is a stepwise process, which often favors the lowest energy reaction channel and does not usually involve the generation of electronic excited states.[10] However, we will give results which show that infrared excitation does allow reactions to proceed in states other than the electronic ground state. Although the total energy taken up by an ion can often be equivalent to that of a single visible photon, stepwise absorption coupled to energy randomization ensures that there is little possibility of localized excitation to any significant degree. Support for efficient energy randomization is provide through an extensive study of reactions involving complexes composed of mixed isotopomers.

Infrared experiments on ions held in an ICR trap were first reported by Beauchamp and co-workers.[10−12] The systems

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(1) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445.
(2) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.
(3) Eller, K.; Schwartz, H. *Chem. Rev.* **1991**, *91*, 1121.
(4) Russell, D. H., Ed. *Gas-Phase Inorganic Chemistry*; Plenum Press: New York, 1989.
(5) Weisshaar, J. C. In *Advances in Chemical Physics*; Ng, C., Ed.; Wiley-Interscience: New York, 1992; Vol. 82.
(6) Freiser, B. S., Ed. *Gas-Phase Organometallic Ion Chemistry*; Kluwer: Dordrecht, The Netherlands, 1996.
(7) Prusse, T.; Schwarz, H. *Organometallics* **1989**, *8*, 2856.
(8) Karrass, S.; Prusse, T.; Eller, K.; Schwarz, H. *J. Am. Chem. Soc.* **1989**, *111*, 9018.
(9) Prusse, T.; Allison, J.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 553.
(10) Woodin, R. L.; Bomse, D. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1979**, *63*, 630.

10.1021/ja980156n CCC: $15.00

studied showed no significant frequency dependence across the range accessible to the $CO_2$ laser, and for the most part, each different complex exhibited a single reaction pathway. Beauchamp and co-workers were also the first to extend this approach to metal ion−molecule complexes, but again no significant frequency dependences were observed and only single reaction channels were present.[13] More recently, Freiser and co-workers have published the results of a series of experiments performed at a single $CO_2$ laser frequency, where competitive reaction channels involving up to four separate product ions were observed.[14] Such behavior can be rationalized in terms of a set of criteria proposed by Brauman and co-workers.[15]

In an earlier publication we reported preliminary results of experiments on the infrared multiphoton excitation of transition metal atoms and small clusters in association with one and two ethanol molecules.[16] A characteristic of these results compared with those recorded in previous infrared experiments is the presence of a very distinct frequency dependence which appears to be associated with an enhanced absorption cross section. Similar behavior has also been reported by both Dietrich *et al.*[17] and Koretsky and Knickelbein.[18]

## Experimental Section

The experiments were performed in a Finnigan MAT Ion Trap Mass Spectrometer (ITMS) in conjunction with an Edinburgh Instruments PL4 $CO_2$ laser operated in pulse mode. The laser beam enters and exits the trap through two 1 mm holes drilled on opposite sides of the central ring electrode: to maintain the integrity of the RF trapping field, the holes are covered with fine metal gauze. Since the ions are confined by an ac voltage of 1.1 MHz this, in conjunction with the presence of $10^{-5}$ mbar of helium, ensures that ions follow trajectories which pass through the center of the trap, giving maximum interaction with the laser beam. For a 1 ms laser pulse, each ion should pass through the beam approximately 1000 times, which for a typical infrared absorption cross section ($\sim 10^{-19}$ cm$^2$) guarantees the absorption of large numbers of photons. The frequency of the laser was continually monitored by diverting a small fraction into a Mackern Instruments spectrum analyzer with a ZnSe beam splitter. Laser energy was monitored at the point of exit from the trap with a Molectron J50 probe connected to a JD500 energy meter.

All complexes of the form $M^+(EtOH)_n$ were prepared by promoting controlled ion−molecule reactions between isolated fragments of ionized metal carbonyls with neutral ethanol molecules. The carbonyls used were $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Co(CO)_3(NO)$, and $Ni(CO)_4$. All were used as purchased without further purification apart from degassing. In addition, the following isotopomers of ethanol were used: $C_2H_5OH$, $CH_3CD_2OH$ (referred to as $d_2$-EtOH), $CD_3CH_2OH$ ($d_3$-EtOH), and $CD_3CD_2OD$ ($d_5$-EtOD). It was also possible to create two further variations: $CD_3CD_2OH$ ($d_5$-EtOH) was generated via hydroxyl D atom exchange with atoms on the internal surfaces of the apparatus, and $C_2H_5OD$ (EtOD) was generated by bleeding the vapor into the trap above a mixture of $D_2O$ and $C_2H_5OH$ held in a reservoir.

**Table 1.** Photoinduced Loss Channels from $Fe^+(d_n\text{-EtOH})_m$ Clusters

| parent ion | ion frag(s) | neutral frag(s) | laser/ mJ |
|---|---|---|---|
| $Fe^+(EtOH)$ | $Fe^+(C_2H_4)$ | $H_2O$ | 1.1 |
| $Fe^+(EtOH)_2$ | $Fe^+(C_2H_4)(EtOH)$ | $H_2O$ | 0.6 |
| $Fe^+(EtOD)$ | $Fe^+(C_2H_4)$ | DOH | 1.4 |
| $Fe^+(EtOD)_2$ | $Fe^+(C_2H_4)(EtOD)$ | DOH | 0.8 |
| $Fe^+(d_2\text{-EtOH})$ | $Fe^+(C_2H_2D_2)$ | $H_2O$ | 1.0 |
| $Fe^+(d_2\text{-EtOH})_2$ | $Fe^+(C_2H_2D_2)(d_2\text{-EtOH})$ | $H_2O$ | 0.9 |
| $Fe^+(d_3\text{-EtOH})$ | $Fe^+(C_2H_2D_2) + Fe^+(C_2HD_3)$ | $DOH + H_2O$ | 1.7 |
| $Fe^+(d_3\text{-EtOH})_2$ | $Fe^+(C_2H_2D_2)(d_3\text{-EtOH}) + Fe^+(C_2HD_3)(d_3\text{-EtOH})$ | $DOH + H_2O$ | 0.7 |
| $Fe^+(d_5\text{-EtOH})$ | $Fe^+(C_2D_4)$ | DOH | 1.7 |
| $Fe^+(d_5\text{-EtOH})_2$ | $Fe^+(C_2D_4)(d_5\text{-EtOH})$ | DOH | 1.5 |
| $Fe^+(d_5\text{-EtOD})$ | $Fe^+(C_2D_4)$ | $D_2O$ | 0.8 |
| $Fe^+(d_5\text{-EtOD})_2$ | $Fe^+(C_2D_4)(d_5\text{-EtOD})$ | $D_2O$ | 0.8 |

## Results and Discussion

As a general observation it is found that, if a metal *n*-carbonyl ion, $[M^+(CO)_n]$, reacts with *n* molecules of ethanol, the resultant product is an adduct of the form $M^+(EtOH)_n$. This is a multistep process with sequential substitution of the carbonyl ligands by the ethanol molecule to liberate CO. The process can be stopped at an intermediate stage and ions of the form $M^+(CO)_m(EtOH)_l$ isolated. For large values of *n* the time scale for complete substitution may be of the order of 1 s, although this value is dependent upon the nature of the metal ion and the partial pressure of ethanol. When *n* is small or 0, the complete loss of carbonyl ligands can be accompanied by an additional reaction, whereby a further ethanol molecule becomes attached to the metal ion via the loss of a hydrogen radical to generate an ethoxide group. This process is observed for iron and manganese cations, but not for chromium, cobalt, or nickel. For these latter ions, the further addition of ethanol ligands occurs without loss of $H^\bullet$, but at rates significantly slower than those observed for direct substitution. Iron and manganese ethoxide ions undergo infrared photodissociation, but exhibit frequency dependences and fragmentation patterns that are entirely different from those seen here. The results of an extensive study of infrared photofragmentation in the iron ethoxide system have been reported separately;[19] however, the significance of ethoxide formation in the context of the present work will be discussed in further detail below.

Results on the multiphoton and collision-induced reactions of $M^+(EtOH)_m$ cluster ions are presented here for $m = 1$ and 2. Data recorded for the chemistry of iron are discussed first as this system has been studied in most detail by both us and other groups. We shall then discuss the effects a change of metal atom has on the behavior of the complexes.

**MPD Photochemistry of $Fe^+(EtOH)_m$.** The primary response of complexes of the form $Fe^+(EtOH)_m$ to infrared photoexcitation can be summarized as follows:

$$Fe^+(EtOH)_m + nh\nu \rightarrow Fe^+(C_2H_4)(EtOH)_{m-1} + H_2O \tag{1}$$

A full list of all the various ion combinations studied together with their fragments is given in Table 1, as are the laser energies required to promote reaction 1 to a point where the maximum fragment yield was ∼50% of the parent ion intensity. The associated fragment ion intensities are plotted as a function of laser frequency in Figure 1. As can be seen, iron ions ligated solely with one or two undeuterated ethanol molecules dehydrate

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[11] Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 3967.

[12] Bomse, D. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 3292.

[13] Hanratty, M. A.; Paulsen, C. M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5074.

[14] Surya, P. I.; Ranatunga, D. R. A.; Freiser, B. S. *J. Am. Chem. Soc.* **1997**, *119*, 3351.

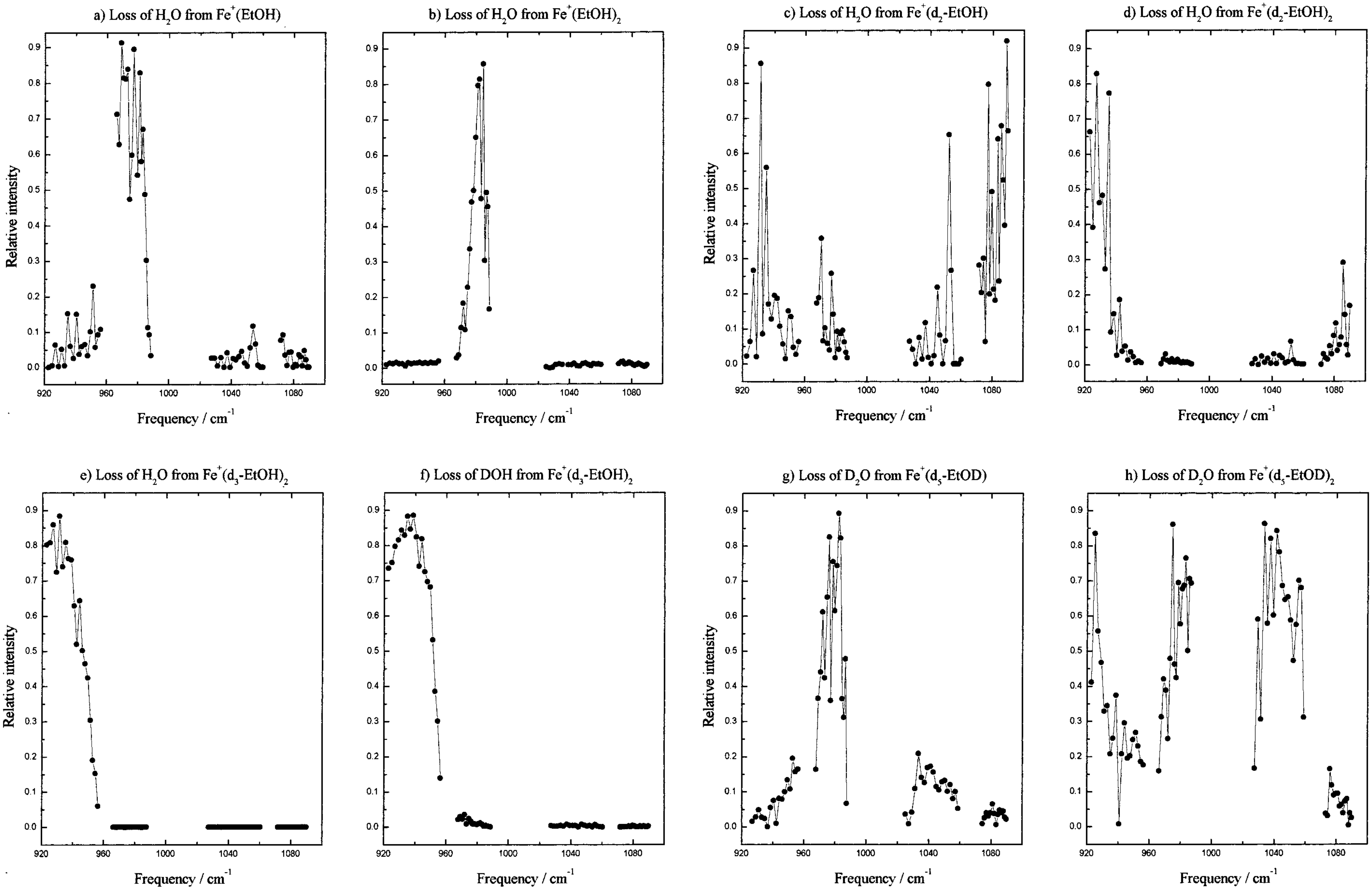
[15] Moylan, C. R.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1985**, *107*, 1394.

[16] Kirkwood, D. A.; Winkel, J. F.; Stace, A. J. *Chem. Phys. Lett.* **1995**, *247*, 332.

[17] Dietrich, G.; Dasgupta, K.; Kruckeberg, S.; Lutzenkirchen, K.; Schweikhard, L.; Walther, C.; Ziegler, J. *Chem. Phys. Lett.* **1996**, *259*, 397.

[18] Koretsky, G. M.; Knickelbein, M. B. *Chem. Phys. Lett.* **1997**, *267*, 485.

[19] Kirkwood, D. A.; Stace, A. J. *Int. J. Mass Spectrom. Ion Processes* **1997**, *171*, 39.



a) Loss of $H_2O$ from $Fe^+(EtOH)$

b) Loss of $H_2O$ from $Fe^+(EtOH)_2$

c) Loss of $H_2O$ from $Fe^+(d_2\text{-}EtOH)$

d) Loss of $H_2O$ from $Fe^+(d_2\text{-}EtOH)_2$

e) Loss of $H_2O$ from $Fe^+(d_3\text{-}EtOH)_2$

f) Loss of DOH from $Fe^+(d_3\text{-}EtOH)_2$

g) Loss of $D_2O$ from $Fe^+(d_5\text{-}EtOD)$

h) Loss of $D_2O$ from $Fe^+(d_5\text{-}EtOD)_2$

**Figure 1.** Relative photofragment intensities recorded for a range of $Fe^+$−ethanol complexes as a function of $CO_2$ laser frequency.

exclusively in the 10R region of the $CO_2$ laser (960−988 $cm^{-1}$). The frequency maximum for $Fe^+(EtOH)$ appears at a slightly lower energy (965 $cm^{-1}$) than that seen for the doubly ligated species, $Fe^+(EtOH)_2$ at 980 $cm^{-1}$; however, almost double the laser energy is required to promote a comparable level of reactivity in the former. This observation regarding laser energy is generally true for all the isotopic combinations presented in Table 1. When a carbonyl group remains attached to an iron/$d_n$-ethanol complex (with either one or two ethanols), the photoproduct changes to carbon monoxide, although the frequency dependence remains largely unchanged (see Figure 2). This observation would imply that the $Fe^+-CO$ bond energy at ∼32 kcal $mol^{-1}$ is weaker than that of $Fe^+-EtOH$. However, direct comparisons may not be valid because of possible changes brought about in the electron configuration of $Fe^+$ when two or more ligands are present in a complex.[20]

All ions given in Table 1 dehydrate upon irradiation. In general the presence of a second ligand does not appear to influence which isotopomers of water are produced, although as will be shown later that it may affect product ratios. Unsubstituted ethanol and $d_2$-EtOH yield $H_2O$ upon irradiation, both EtOD and $d_5$-EtOH generate DOH, and $d_5$-EtOD yields $D_2O$, all of which conform to the mechanism established for dehydration.[1,2] In the case of $d_3$-ethanol, however, the situation is quite different, with both ions $Fe^+(d_3\text{-EtOH})_{1,2}$ losing DOH *and* $H_2O$. The ratio of the products DOH:$H_2O$ is 1.84:1 for the monoligated ion but drops to 1.17:1 in the case of $Fe^+(d_3\text{-EtOH})_2$.

The frequency dependences of infrared-induced dehydration shown by the various iron/ethanol ion complexes are also given in Figure 1. There is no result for $Fe^+(d_3\text{-EtOH})$ due to the propensity of this ion to undergo further rapid ion−molecule reactions with background ethanol to produce more highly solvated species. Instead, profiles for the separate loss channels of $Fe^+(d_3\text{-EtOH})_2$ are displayed. From the eight plots it is evident that some of the observed spectra show strong dependences both on the number of alcohol molecules present and on the degree of isotopic substitution. Thus, while $Fe^+(EtOH)_1$ and $Fe^+(EtOH)_2$ exhibit similar profiles, this is not the case when the alcohol is in the form of either $d_2$-EtOH or $d_5$-EtOD. For fully deuterated ethanol, the single ligand complex has a profile similar to that seen for EtOH, while that of the doubly ligated ion is more complex. The profile of $Fe^+(d_2\text{-EtOH})$ appears complex because this ion has a comparatively low photofragmentation efficiency over the accessible frequency range, and this results in a poor signal-to-noise ratio. The profile recorded for $Fe^+(EtOD)$ (not shown) is similar to that of $Fe^+(EtOH)$, but with additional photofragmentation features between 920 and 950 $cm^{-1}$. A contributing factor to the increased complexity of spectra when deuterated alcohols are used is the high density of vibrational energy levels, which for large molecules or complexes would ultimately result in photodissociation processes being frequency independent.

As a preliminary to investigating the dehydration mechanism it would be useful at this stage to discuss which of the infrared active modes in these complexes may be responsible for excitation and subsequent dissociation. For an isolated ethanol molecule, both the C−O stretch ($\nu_a$(CCO) asymmetric stretch mode at 1057 $cm^{-1}$) and the $CH_3$ rock (in and out of plane at ∼1030 and ∼1080 $cm^{-1}$, respectively) have absorption frequen-

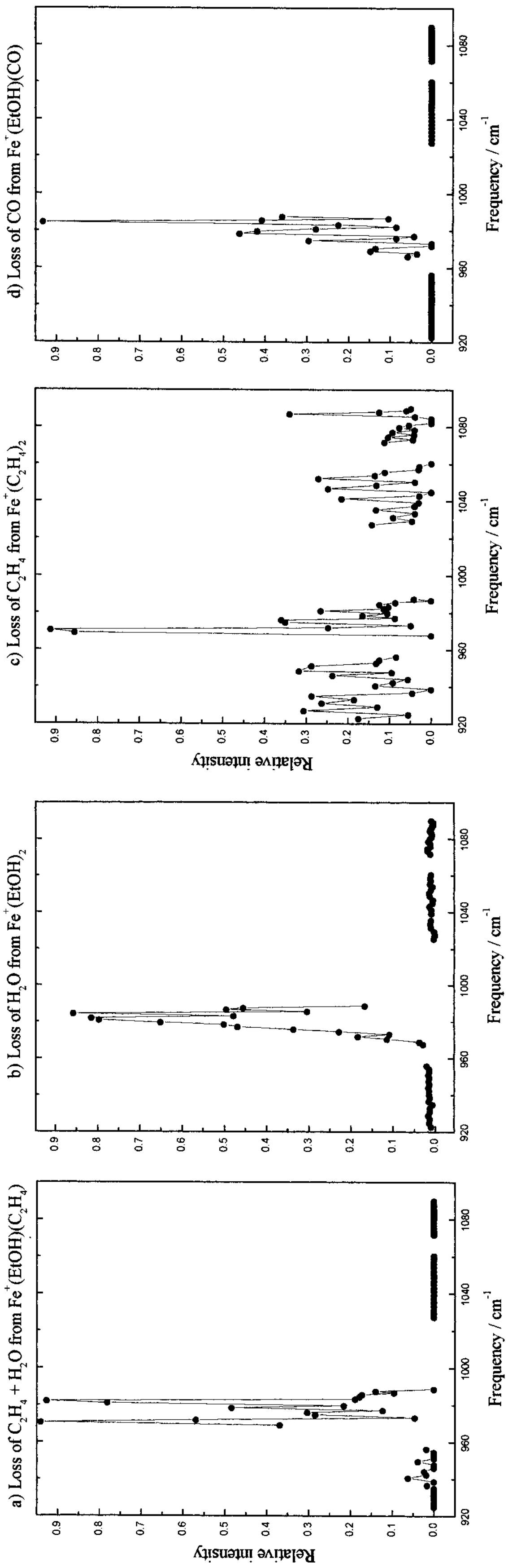


**Figure 2.** As for Figure 1, but exploring the influence of additional ligands in the form of CO and $C_2H_4$.

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[20] Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. In *Gas-Phase Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; Chapter 2.

cies which lie within the range of the $CO_2$ laser.[21,22] However, since neither of these can immediately be equated with the pattern of behavior seen in Figure 1, it might also be necessary to include in the list the symmetric CCO stretch, $\nu_s$(CCO), at 880 $cm^{-1}$. In their analysis of the reaction between $Fe^+$ and ethanol, Ridge *et al.*[2] proposed that the initial insertion step associated with dehydration was spontaneous, and that the stoicheometric ion $Fe^+$(EtOH) was in fact $(C_2H_5)Fe^+(OH)$. Such a step would clearly preclude either $\nu_a$(CCO) or $\nu_s$(CCO) from being the chromophore in these ions. Alternative suggestions have included the iron hydride cation as a possible chromophore (the formation of an $Fe^+-H$ bond being an intermediate step in the dehydration reaction).[23] However, separate experiments have demonstrated that $Fe^+-H$ does not absorb infrared radiation within the range accessible from a $CO_2$ laser.[24] An examination of reaction 1 would suggest that the only other possible candidate is $C_2H_4$, which is known to have a strong infrared transition ($\nu_7$) at ~948 $cm^{-1}$. The implication then would be that the entire dehydration reaction proceeds very rapidly, and that infrared absorption merely facilitates separation of the reaction products. In an attempt to resolve this issue the following ions were prepared and irradiated: $Fe^+(EtOH)_2$, $Fe^+(C_2H_4)_2$ (from the gas-phase reaction between ethene and $Fe^+(CO)_2$), and $Fe^+(EtOH)(C_2H_4)$ (from the CID of $Fe^+(EtOH)_2$). The photofragmentation spectra recorded for these ions are shown in Figure 2.

From Figure 2 it can be seen that the profile recorded by monitoring the dehydration of $Fe^+(EtOH)_2$ is approximately Gaussian with a center of absorption lying at ~983 $cm^{-1}$. The ion $Fe^+(EtOH)(C_2H_4)$, which yields both $H_2O$ *and* $C_2H_4$ on irradiation, has maxima at 983 and 970 $cm^{-1}$; the poor signal-to-noise ratio is a consequence of a low parent ion intensity. When the laser-induced loss of $C_2H_4$ from $Fe^+(C_2H_4)_2$ is examined, the profile is found to consist of a single narrow peak centered at 970 $cm^{-1}$, which corresponds exactly to the second peak seen for $Fe^+(EtOH)(C_2H_4)$. This observation, coupled to the fact that $Fe^+(EtOH)_{1,2}$ ions are not found to lose $C_2H_4$ upon photoexcitation, would imply that $C_2H_4$ does not act as a chromophore, and that parent ions are not of the form $(C_2H_4)$-$Fe^+(H_2O)$ prior to excitation with laser radiation. Additional chemical evidence to exclude $C_2H_4$ as the chromophore is presented below.

Of the two remaining possible chromophores, the C−O stretch and the $CH_3$ rock, evidence in favor of the former comes from earlier work by Zakin *et al.*[23] on infrared depletion studies of neutral $Fe_n(MeOH)_m$ clusters. They observed two strong absorption features, with that at 985 $cm^{-1}$ being attributed to chemisorbed methoxy, and comparisons were made with results from bulk surface spectral measurements. Further evidence in support of the C−O stretch comes from a consideration of the structure of the $Fe^+$(EtOH) complex. The most appropriate bonding configuration would appear to be attachment of the hydroxyl oxygen atom to the metal ion. The lone pair electrons on the oxygen atom would contribute to the molecule being a donor ligand, whereas the metallic cation, being electron deficient, would act as an electron acceptor (a Lewis acid−Lewis base arrangement). A similar situation arises when alcohol molecules are attached to bulk ionic surfaces, such as those of NiO and $TiO_2$, and where the net result is an enhancement of the spectral absorption intensity of the C−O stretch at ~1080 $cm^{-1}$.[25,26] Unlike the bulk surface measurements, the results for $Fe^+$(EtOH) are either red-shifted with respect to $\nu_a$(CCO) or blue-shifted with respect to $\nu_s$(CCO). Since the effect of the positive charge will be to withdraw electron population from the C−O bond, a red shift is more probable, which would be consistent with observations made on methanol molecules absorbed on the surfaces of pure metals.[26] A point in favor of the $CH_3$ rock as chromophore is the pronounced variation seen in Figure 1 as a function of isotopic substitution. A simple empirical calculation of the expected frequency shift for the $CH_3$ rock on going from $Fe^+$(EtOH) to $Fe^+$($d_3$-EtOH) would place the absorption maximum for the latter at ~915 $cm^{-1}$ as opposed to ~930 $cm^{-1}$ as seen in Figure 1. It will be seen later that a comparable change of mass, but on the part of the metal atom, has almost no effect on the frequency dependence of photofragmentation when compared with $Fe^+$(EtOH).

A separate study of iron−ethoxide cations, $Fe^+$(EtO)(EtOH), revealed the presence of strong absorption features centered at ~1060 $cm^{-1}$,[19] which were independent of the degree of isotopic substitution and characteristic of a $\nu$(C−O) stretching frequency for a surface-bound alkoxide.[27] The difference between $Fe^+$(EtO) and $Fe^+$(EtOH) is that the former probably contains a covalent bond between the radical and $Fe^+$ in the electronic ground state. In contrast, $Fe^+$(EtOH) will be an ion−dipole complex and $Fe^+$ is probably in the first excited electronic state (see below). Clearly, these two different bonding configurations will influence the vibrational frequency of the C−O bond.

It is quite probable that the observed frequency dependences are composed of varying mixtures of all active vibrational modes, and that one or more may dominate depending on the level of frequency shift experienced as a result of isotopic substitution. Experiments by Bomse and Beauchamp[10] showed that the proton-bound ethanol dimer ion has a broad featureless absorption profile in the infrared and yields mainly $H_2O$ as a reaction product. It is clear, therefore, that the replacement of $H^+$ by $Fe^+$ has a significant influence on the chromophore, and that this pattern of behavior is a characteristic of all the metal ions studied thus far (see below). What also appears to be clear is that ethanol remains intact prior to photoexcitation. Additional evidence in support of this conclusion is discussed later.

The ion−molecule reaction mechanism for the dehydration of ethanol by $Fe^+$ is well-established, and is accepted to be a two-step scheme that commences with metal insertion into the C−O bond and concludes with $\beta$-hydrogen transfer.[1,2] The end result is an ion−dipole complex between $Fe^+$ and water and a $\pi$−d bonded ethene molecule. Since the water molecule appears to be the more weakly bound of the two product molecules, any excess energy causes this species to be lost, leaving $Fe^+(C_2H_4)$. These steps are displayed in Scheme 1, and a potential energy surface for the reaction is presented in Figure 3. This diagram is based largely on the surface devised by Ridge and Allison,[2] the main modification being the addition of a minimum corresponding to a bound state for the ion complex, where $Fe^+$ is bonded to ethanol by ion−dipole and ion-induced dipole interactions *prior to insertion*. In this respect, an upper limit to the expected binding energy ($D_0$) might be obtained from a consideration of measurements by Freiser *et al.*[28] on

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[21] Perchard, J.-P.; Josien, M.-L. *J. Chim. Phys. Physicochim. Biol.* **1968**, *65*, 1834 and 1856.

[22] Barnes, A. J.; Hallam, H. E. *Trans. Faraday Soc.* **1970**, *66*, 1932.

[23] Zakin, M. R.; Brickman, R. O.; Cox, D. M.; Reichmann, K. C.; Trevor, D. J.; Kaldor, A. *J. Chem. Phys.* **1986**, *85*, 1198.

[24] Kirkwood, D. A. D. Phil. Thesis, University of Sussex, 1996.

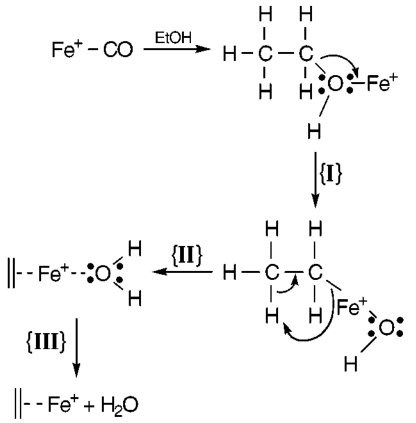
[25] Hussein, G. A. M.; Sheppard, N.; Zaki, M. I.; Fahim, R. B. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2661.

[26] Wu, M.-C.; Truong, M.; Goodman, D. W. *J. Phys. Chem.* **1993**, *97*, 9425.

[27] Dubicki, L; Kakos, G. A.; Winter, G. *Aust. J. Chem.* **1968**, *21*, 1461.

[28] Operti, L.; Tews, E. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1988**, *110*, 3847.

**Scheme 1**



$Mg^+{-}L$ complexes, where for $L = C_2H_5OH$, $D_0$ is 2.7 eV (~25 infrared photons). A lower limit to $D_0$ would be either the experimental[29] or calculated[30] binding energy of $Fe^+{-}H_2O$ at between 1.32 and 1.44 eV (~12 infrared photons). The water molecule has a higher dipole moment than ethanol, but a lower polarizability. Additional data on metal ion−molecule binding energies can be found in ref 31.

At this stage it is instructive to place some of the above observations in the context of a molecular orbital analysis of the photoinduced reaction of $Fe^+$. Much of this discussion is derived from a range of very comprehensive studies of the reactions of excited-state metal ions by Armentrout and co-workers,[32−37] Weisshaar,[5] and Bowers and co-workers.[38] We begin with the qualitative observation that when bare $Fe^+$ reacts with ethanol then the outcome is

$$Fe^+ + C_2H_5OH \rightarrow Fe^+OC_2H_5 + H \qquad (2)$$

This compares with the process that takes place when $Fe^+CO$ is the reactant ion

$$Fe^+CO + C_2H_5OH \rightarrow Fe^+HOC_2H_5 + CO \qquad (3)$$

Apart from the fact that a bimolecular exchange reaction, such as (3), will allow excess energy to be dissipated in the form of kinetic and internal energy on the part of CO,[1,2] the most significant difference between reactions 2 and 3 is the electronic state of $Fe^+$. The ground state of the atomic iron ion is $^6D(4s^1 3d^6)$; in contrast calculations show the ground state of $Fe^+CO$ to be $^4\Sigma^-$, which correlates with the $^4F(3d^7)$ excited state of $Fe^+$ at the dissociation asymptote.[39] Thus, $Fe^+$ (assumed to be predominately in the ground state) quite readily undergoes an exothermic reaction with ethanol in much the same that it does with propane at low relative kinetic energies[33,38] (it is acknowledged that there is not the same level of control over kinetic energy in the ion trap as there is in a guided ion beam apparatus). With ethanol, the preferred reaction is direct H−O insertion to yield $Fe^+OC_2H_5$, whereas with propane both C−H and C−C insertion are observed.[33,38] Similar reaction pathways have recently been observed by Baranov *et al.*[40] in a drift-tube study of the reactions of ground-state $Fe^+$.

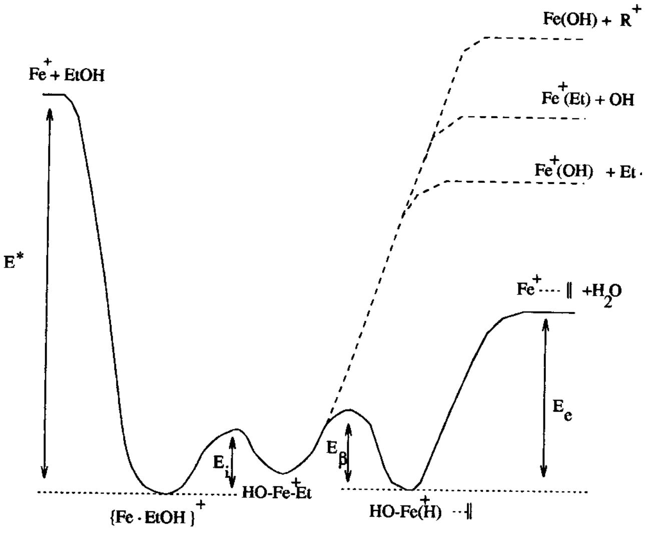


**Figure 3.** Potential energy contour for the dehydration of $Fe^+{-}$ethanol. Adapted from ref 2, but making allowance for the metal−ligand bond energy.

In the exchange reaction, (3), we believe that $Fe^+$ retains the $^4F(3d^7)$ electronic configuration of the excited state, and it is this that is responsible for the observed dehydration reaction pathway (Scheme 1). The fact that the ion complex is stable in the absence of infrared excitation would again be consistent with the observations of Armentrout and co-workers on hydrocarbons.[33] These authors attributed the kinetic energy dependence of $Fe^+$ $^4F(3d^7)$ reactivity to a barrier imposed by a surface crossing.[33] A second important consideration from earlier work is the nature of the bonding in the reaction intermediate: $HO{-}Fe^+{-}C_2H_5$. If this insertion step requires the formation of two covalent bonds, this would best be achieved by electron donation into an empty 4s orbital, as found in the first excited state of $Fe^+$. In contrast, if $Fe^+$ were in the electronic ground state, then the partially occupied 4s orbital would present a repulsive interaction to the donating $\sigma$ electrons of the $HO^\bullet$ and $^\bullet C_2H_5$ radicals. A final point of interest in this section concerns the eventual break up of the product complex: $H_2O{-}Fe^+{-}C_2H_4$. A consensus of the available experimental data on binding energies[31] gives a value of ~31 kcal $mol^{-1}$ for $Fe^+{-}H_2O$ and ~35 kcal $mol^{-1}$ for $Fe^+{-}C_2H_4$, which would account for the preferred loss of $H_2O$. However, the pattern of behavior could be slightly more subtle in that the lowest energy state of $Fe^+{-}H_2O$ is predicted to be $^6A_1$,[30] but for $Fe^+{-}C_2H_4$ the same calculations show the lowest energy state as $^4B_2$.[41] Thus, it would be possible to envisage the entire reactive process proceeding on a surface which correlates with the $^4F(3d^7)$ state of $Fe^+$ at one of the dissociation asymptotes. The one slight drawback in this picture is that the same calculations also show that for both electronic states of the iron cation, water is more strongly bound than ethene in complexes with a single ligand. The experiments clearly demonstrate that this is not the case;

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(29) Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519.

(30) Rosi, M.; Bauschlicher, C. W. *J. Chem. Phys.* **1990**, *92*, 1876.

(31) See, for example: *Gas-Phase Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; p 296.

(32) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1987**, *91*, 2037.

(33) Schultz, R. H.; Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 411.

(34) Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1992**, *114*, 2049.

(35) Kickel, B. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 764.

(36) Tjelta, B. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 5531.

(37) Armentrout, P. B. *Annu. Rev. Phys. Chem.* **1990**, *41*, 313.

(38) van Koppen, P. A. M.; Kemper, P. R.; Bowers, M. T. *Gas-Phase Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1996; p 157 and references therein.

(39) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *93*, 609.

(40) Baranov, V.; Becker, H.; Bohme, D. K. *J. Phys. Chem.* **1997**, *101*, 5137.

(41) Sodupe, M.; Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H. *J. Phys. Chem.* **1992**, *96*, 2118, 5760.

**Table 2.** Relative Photodissociation Efficiencies of the $Fe^+(d_n\text{-EtOD})_m$ Clusters

| isotopomer | eff rel to ethanol |
|---|---|
| $CH_3CH_2OH$ | 1.0 |
| $CH_3CD_2OH$ | 0.06 |
| $CD_3CH_2OH$ | 5.2 |
| $CD_3CD_2OD$ | 4.0 |

however, what is required are calculations which show how the $\pi$−d bonding between $Fe^+$ and ethene influences the energetics of the interaction between $Fe^+$ and water.

In the case of dimer complexes, i.e., $Fe^+(EtOH)_2$, the situation is slightly more straightforward: using $Fe^+(H_2O)_2$ as an analogue, then calculations on this ion show the most stable configuration to be linear with $Fe^+$ correlating as $^4F(3d^7)$.[30,42] Ligand−ligand repulsion is partly responsible for this change compared with $Fe^+H_2O$, and that effect is likely to be even more pronounced for $Fe^+(EtOH)_2$. Hence all dimer reactions could proceed on a surface that keeps $Fe^+$ in the first excited state, and this, in part, may account for the marked increase in fragment ion yield derived from dimer complexes when compared with that obtained when only one alcohol molecule is present.

If Scheme 1 is applied to the photodehydration of each of the isotopomers of ethanol, then it may be seen from Table 1 that all reactions are accounted for, except those displayed by $Fe^+(d_3\text{-EtOH})$. The loss of $H_2O$ from this ion cannot be explained by the simple mechanism given in Scheme 1. Although there have been no comparable studies which cover all of the isotopomers presented here, Allison and Ridge[2] did observe that the alkyl halide $CD_3CH_2I$ lost both DI and HI in the ratio 3:2 upon reaction with $Fe^+$. From a consideration of Scheme 1 (it is generally considered that the scheme is appropriate for both alkyl alcohols and halides), $CD_3CH_2I$ would be expected to lose only DI, and the apparent discrepancy was interpreted as evidence of an exchange reaction between the H atom transferred to $Fe^+$ and the hydrogen atoms remaining on the ethene ligand. For an ethene molecule free to rotate about the $\pi$−$Fe^+$ bond, the equivalent mechanism in an $Fe^+(CD_3CH_2OH)$ complex would be

$$(C_2H_2D_2)Fe^+(D)(OH) \leftrightarrow (C_2HD_3)Fe^+(H)(OH) \qquad (2)$$

Unfortunately, no data are available for the corresponding reaction between $Fe^+$ and $CH_3CD_2I$, which on the above analysis would be expected to yield DI and HI in the ratio 2:3. An application of the above interpretation to the systems studied here is considered inappropriate for several reasons. First, the ion $Fe^+(d_2\text{-EtOH})$ exhibits no propensity to yield DOH upon either infrared irradiation or collisional activation. Second, the ratio of DOH to $H_2O$ loss from $Fe^+(d_3\text{-EtOH})$ is 1.8:1, which is different from the anticipated 1.5:1, and finally when a second $d_3$-ethanol is added to the ion, this ratio drops to 1.2:1. A more likely interpretation for the appearance of $H_2O$ from $Fe^+(CD_3CH_2OH)$ is that the proton ligated to the iron ion undergoes exchange with hydroxyl protons from neutral ethanol molecules within the trap. The change in ratio with two ligands comes about as a result of the slightly higher ethanol pressure required to attach two molecules.

Finally in this section, it is worth noting that the photofragmentation patterns of the ions $Fe^+(d_2\text{-EtOH})_2$ and $Fe^+(d_3\text{-EtOH})_2$ exhibit markedly different frequency dependences, which again precludes ethene as the chromophore in these ions as both complexes yield $C_2H_2D_2$ upon $\beta$-hydrogen transfer.

**Ions Containing Mixed Isotopomers of Ethanol in Association with $Fe^+$.** From the information provided in Figure 1 and Table 1 it is clear that while each different isotopomer of ethanol yields water as a photofragment when attached to the $Fe^+$ cation, the dependence of this process varies with the degree of isotopic substitution. This observation raises the intriguing question as to what should be expected if two different $d_n$-EtOH ligands are irradiated on a single cation. For example, should mode-dependent chemistry be expected?

Figure 4 shows the results of four separate experiments where the following combinations were irradiated: $Fe^+(EtOH)(EtOD)$, $Fe^+(EtOH)(d_2\text{-EtOH})$, $Fe^+(EtOH)(d_3\text{-EtOH})$, and $Fe^+(EtOH)(d_5\text{-EtOD})$. The method of preparation was slightly different from that described above. The unsubstituted alcohol was bled into the trap continuously with the iron pentacarbonyl, and after ionization the species $Fe^+(EtOH)(CO)$ was isolated. The $d_n$-alcohol of choice was then pulsed into the trap through a Jordan nozzle (∼200 $\mu$s gas pulse) and sufficient reaction time allowed to generate quantitative amounts of the desired $Fe^+(EtOH)(d_n\text{-EtOH})$ complex.

The data shown in Figure 4 reveal a number of features that would have been anticipated from previous results. The fragmentation pattern of $Fe^+(EtOH)(d_2\text{-EtOH})$ is much as expected, with the ion losing only $H_2O$. However, the frequency dependence is dominated by features associated with the unsubstituted alcohol, and only a small amount of product appears at frequencies where $d_2$-ethanol is expected to absorb. Such behavior will be influenced by differences in the infrared absorption cross sections of the two alcohols concerned. For the complex $Fe^+(EtOH)(d_3\text{-EtOH})$ two loss channels, $-H_2O$ and −DOH, are expected, and indeed observed. Both channels have virtually identical frequency dependences, with strong features in both the 10P and 10R branches of the laser. A comparison with Figure 1 shows that there are contributions from both alcohols, and because each absorbs in a separate laser region, the ratio of the integrated intensities of the two spectral features at 5.17:1 provides a measure of the relative photodissociation efficiencies. The other point of major interest is the $H_2O$:DOH isotope ratio which is ∼2.4:1 and extends across the frequency range. This aspect of the results will be discussed later. Identical frequency dependences were also observed for the loss of $H_2O$ and DOH from the complex $Fe^+(EtOH)(EtOD)$. Although the ion *appears* to lose more $H_2O$ than DOH, a correction has to be made for an underlying contribution arising from the loss of DOH by $Fe^+(EtOD)_2$, which is mass coincident with the ion formed by loss of $H_2O$ from $Fe^+(EtOH)(EtOD)$. The frequency dependence is dominated by the 10R contribution from EtOH, with little or no evidence of any 10P absorption by EtOD. The product isotope ratio is 1:1.

The final mixed ion to be examined was $Fe^+(EtOH)(d_5\text{-EtOD})$, which also yields two photofragments, $H_2O$ and $D_2O$, and again the frequency dependences of both were almost identical. The calculated isotope ratio should be 1:1, but the signal for $H_2O$ loss is approximately twice that of $D_2O$. Although both isotopomers have strong absorption features in the 10R laser branch, only $C_2D_5OD$ absorbs in the 9R region, from which the relative photodissociation efficiencies of EtOH and $d_5$-EtOD could be estimated as 1:3.82. A further measurement made on this particular system examined the power dependencies of the two decay channels. This showed that the elimination of $D_2O$ required 5.7 photons as opposed to only 3.9 photons for $H_2O$, a ratio of 1.5:1. Such a trend is characteristic of a primary

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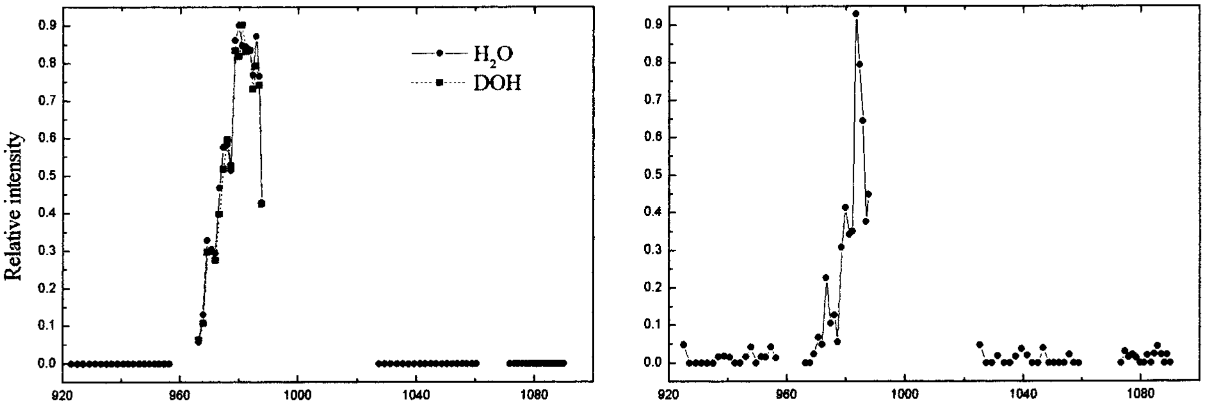
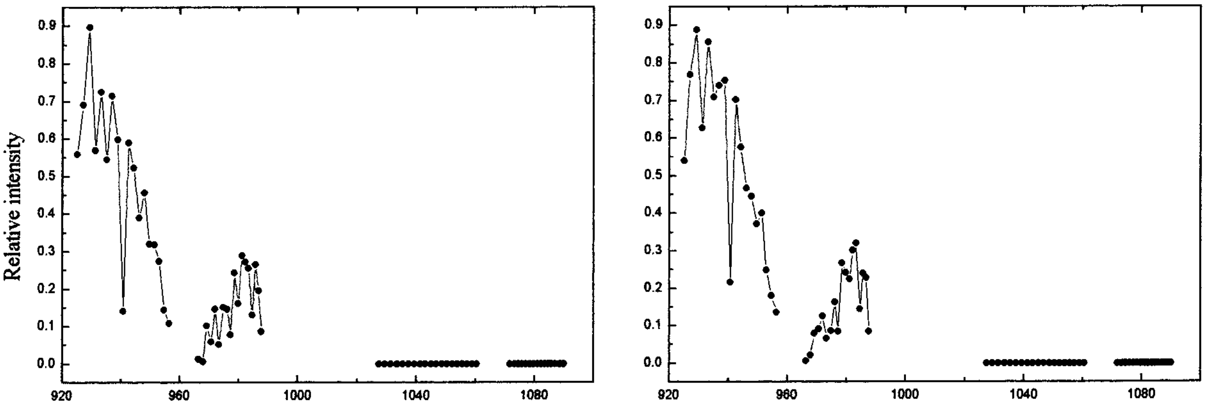
[42] Rosi, M.; Bauschlicher, Jr., C. W. *J. Chem. Phys.* **1989**, *90*, 7264.

a) Loss of $H_2O$ and DOH from $Fe^+(EtOH)(EtOD)$ b) Loss of $H_2O$ from $Fe^+(EtOH)(d_2\text{-}EtOH)$



c) Loss of DOH from $Fe^+(EtOH)(d_3\text{-}EtOH)$ d) Loss of $H_2O$ from $Fe^+(EtOH)(d_3\text{-}EtOH)$



e) Loss of $D_2O$ from $Fe^+(EtOH)(d_5\text{-}EtOD)$ f) Loss of $H_2O$ from $Fe^+(EtOH)(d_5\text{-}EtOD)$

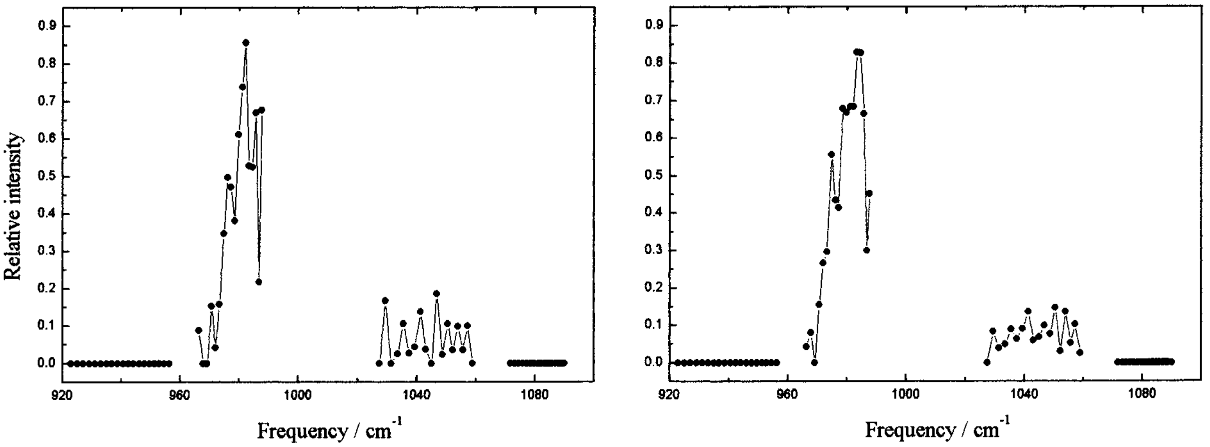


**Figure 4.** As for Figure 1, but recorded for complexes consisting of mixed isotopomers.

isotope effect where a D−R bond is deemed stronger that a H−R bond by virtue of differences in zero-point energy.[43] However, a separate theoretical study of infrared photodissociation in an ion trap[44] reveals the trap to be a very complex environment where variables, including gas pressure, laser fluence, radiative lifetime, and absorption cross-section, have a strong influence on the outcome of laser excitation.[45] Thus, for example, reactions with critical energies equivalent to 12 photons from a $CO_2$ laser can actually require an ion to absorb upward of 20 photons before being promoted.[44] Thus, although power-dependence measurements have been undertaken on some of the processes discussed above, quantitative comparisons between dissimilar alcohol-based systems may not be valid because of differences in absorption cross-section and/or radiative lifetime; however, a difference, such as that seen above for the loss of $D_2O$ and $H_2O$ from the same ion, $Fe^+(EtOH)$($d_5$-EtOD), may not be absolute, but could still reflect the effect of isotopic substitution.

Table 2 presents a summary of relative photodissociation efficiencies with respect to ethanol ($C_2H_5OH$). As can be seen, $CH_3CD_2OH$ proves to be the least efficient chromophore, with a relative efficiency that is a factor of ~15 less than that of the

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[43] Laidler, K. *Chemical Kinetics*; McGraw-Hill: New York, 1965; p 92.

[44] Stace, A. J. *J. Chem. Phys.* In press.

[45] March, R. E.; Hughes, R. J. *Quadrupole storage mass spectrometry*; Wiley: New York, 1985.

**Table 3.** Isotopic Branching Ratios from MPD[a] and CID[b] Experiments on $Fe^+(EtOH)(d_n\text{-}EtOH)$ Ions

| parent ion | neutral products | expected ratio | obsd ratio |
|---|---|---|---|
| $Fe^+(EtOH)(EtOD)$ | $H_2O + DOH$ | 1:1 | 1:1[a] |
| $Fe^+(EtOH)(EtOD)$ | $H_2O + DOH$ | 1:1 | 1.4:1[b] |
| $Fe^+(EtOH)(d_3\text{-}EtOH)$ | $H_2O + DOH$ | 2.1:1[c] | 2.5:1[a] |
| $Fe^+(EtOH)(d_5\text{-}EtOH)$ | $H_2O + DOH$ | 1:1 | 1.5:1[b] |
| $Fe^+(EtOH)(d_5\text{-}EtOD)$ | $H_2O + D_2O$ | 1:1 | 2.5:1[a] |
| $Fe^+(EtOH)(d_5\text{-}EtOD)$ | $H_2O + D_2O$ | 1:1 | 2.3:1[b] |

[a] Multiphoton excitation. [b] Collision-induced dissociation. [c] Includes a correction for the exchange process discussed in the text.

**Table 4.** Photoinduced Processes from $M^+(EtOH)_m$ Ions, for M = Cr, Mn, Co, and Ni

| parent ion | ion product(s) | neutral product(s) |
|---|---|---|
| $Cr^+(EtOH)$ | $Cr^+$ | EtOH |
| $Cr^+(EtOH)_2$ | $Cr^+(EtOH)$ | EtOH |
| $Mn^+(EtOH)$ | $Mn^+$ | EtOH |
| $Co^+(EtOH)$ | $Co^+(C_2H_4)$ | $H_2O$ |
| $Co^+(EtOH)_2$ | $Co^+(C_2H_4)(EtOH)$ | $H_2O$ |
| $Ni^+(EtOH)_2$ | $Ni^+(EtOH) + Ni^+(C_2H_4)(EtOH)$ | $EtOH + H_2O$ |

other alcohols. Part of this effect may be due to the influence isotopic substitution has on the frequencies of those modes responsible for strong absorption, as in some cases, the most active modes may be shifted out of range of the laser. Surjasasmita and Freiser observed that isotopic substitution leads to similar variations in photodissociation yield in $Co^+$/acetone complexes.[46]

The relative photodissociation efficiencies are independent of which photofragment is examined, i.e., $-H_2O$, $-DOH$, or $-D_2O$. However, a second important series of measurements to emerge from the mixed isotope experiments are isotope effects, which do influence the ratios of the above products. The recorded data are summarized in Table 3, where comparisons are made between measurements taken following both multiphoton excitation and collisional activation. The results for $Fe^+(EtOH)(d_3\text{-}EtOH)$ as examined first. This system is made complicated by the fact that earlier results showed that D/H exchange takes place in association with product formation. By using results given above as a measure of the expected level of exchange, an estimate of the expected isotope ratio is 2.1:1, which is slightly below that observed. Likewise, the combination $Fe^+(EtOH)(EtOD)$ yields a ratio that is in line with expectations; the CID result is probably within experimental error given the vagaries of that particular excitation method. The most surprising observations come from the last three results shown in Table 3. The multiphoton excitation of $Fe^+(EtOH)(d_5\text{-}EtOD)$ yields relative signal strengths for the loss of $H_2O$ and $D_2O$ that are almost identical in both the 10R (2.46:1) and 9P (2.48:1) regions of the $CO_2$ laser. This result again supports the assumption that energy is completely randomized before any reactions take place. The average ratio of 2.47:1 in favor of $H_2O$ is completely unexpected, because with each water molecule coming from a totally different reaction site, the ratio should be 1:1. Since there is no evidence of any HOD, we can be confident that exchange reactions are not taking place, and therefore, it must be assumed that the isotope effect reflects subtle differences in bond energies and/or kinetics. In general, the magnitude of the observed isotope effect increases with the level of D/H substitution, which would suggest a secondary effect arising from increased densities of energy states.[43]

**The Reactions of Ions Containing $Mn^+$, $Ni^+$, $Co^+$, and $Cr^+$ in Association with Ethanol.** With the extension of these experiments to other first-row transition metals a number of new and interesting results are obtained. The metals can be crudely split into those which dehydrate ethanol and those which do not. Chromium and manganese fall into the latter category, while cobalt and nickel exhibit a more varied photochemistry, which together with iron includes the dehydration reaction. The picture becomes much more complex when 2nd-row transition metals are studied.[24] For example, the molybdenum cation dehydrogenates ethanol upon infrared excitation, but only undergoes ligand cleavage when activated by collision. A detailed discussion of these results will be presented elsewhere.[47]

Table 4 presents a list of photofragments for a range of ions of the general form $M^+(EtOH)_{1,2}$. In all cases, collisional activation yields the same range of product ions. Both nickel and cobalt show a tendency to lose intact ethanol molecules in competition with dehydration, but for chromium and manganese the only observed photoinduced process is a breaking of the metal ion−ligand bond. Iron complexes show no evidence of photoinduced ligand loss.

A very interesting picture emerges when the frequency dependencies of the various photodissociation processes are examined. The results displayed in Figure 5 show that regardless of the metal ion present or the photoinduced loss channel (ligand cleavage or dehydration) the ions $M^+(EtOH)$ all have frequency dependences centered at ~970 $cm^{-1}$, while the ions $M^+(EtOH)_2$ have maxima at ~983 $cm^{-1}$. There are no data for $Mn^+(EtOH)_2$ as the ionization of dimanganese decacarbonyl does not produce any $Mn^+(CO)_2$, and the reaction of two molecules of ethanol with either $Mn^+$ or $Mn^+(CO)$ generates only the alkoxide species $Mn^+(EtOH)(EtO)$. What is particularly interesting about Figure 5 is the fact that the mass of the metal ion changes from *m/z* 52 for $Cr^+$ to *m/z* 58 for $Ni^+$ without any noticeable change in the absorption frequency. However, as already noted, a comparable increase in mass on the part of an ethanol molecule can cause a very significant change in behavior (compare for example the profiles for $Fe^+(EtOH)_2$ and $Fe^+(d_2\text{-}EtOH)_2$ in Figure 1). This mixture of ligand loss and dehydration reactions, together with the very similar frequency dependencies, once again lends support to the argument that the ions prior to excitation consist of an adduct of each metal bound to an alcohol via ion−dipole and induced dipole interactions, with the point of physical attachment probably being to the lone pair electrons on the oxygen atom.

As seen from the pattern of behavior displayed by $Fe^+$, an important consideration with regard to reactivity is the electron configuration of the metal ion. For all of the metals studied here Table 5 lists configurations for the ground electronic state and any relevant low-lying excited states together with their energies with respect to the ground state. In each case the latter values correspond to the lowest lying *J*-level. Of relevance to an earlier discussion concerning the behavior of bare $Fe^+$ with respect to ethanol is the observation that $Mn^+$ also reacts with ethanol to form an alkoxide, while the other metal ions listed, $Ni^+$, $Co^+$, and $Cr^+$, do not. A reaction between a single molecule of ethanol and the bare metal ion can lead to $Mn^+OC_2H_5$, and when $Mn^+(CO)$ reacts with two molecules of ethanol the result is $Mn^+OC_2H_5(EtOH)$. The pattern of behavior of $Mn^+$ and $Mn^+(CO)$ is slightly different from that seen for $Fe^+$ and $Fe^+(CO)$, but can be rationalized in terms of calculations by Bauschlicher and co-workers.[39] Their results suggest that an excited state of the manganese ion [$^5D$ ($3d^6$)] can be stabilized

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(46) Surjasasmita, P. I.; Freiser, B. S. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 135.

(47) Kirkwood, D. A.; Stace, A. J. To be submitted for publication.

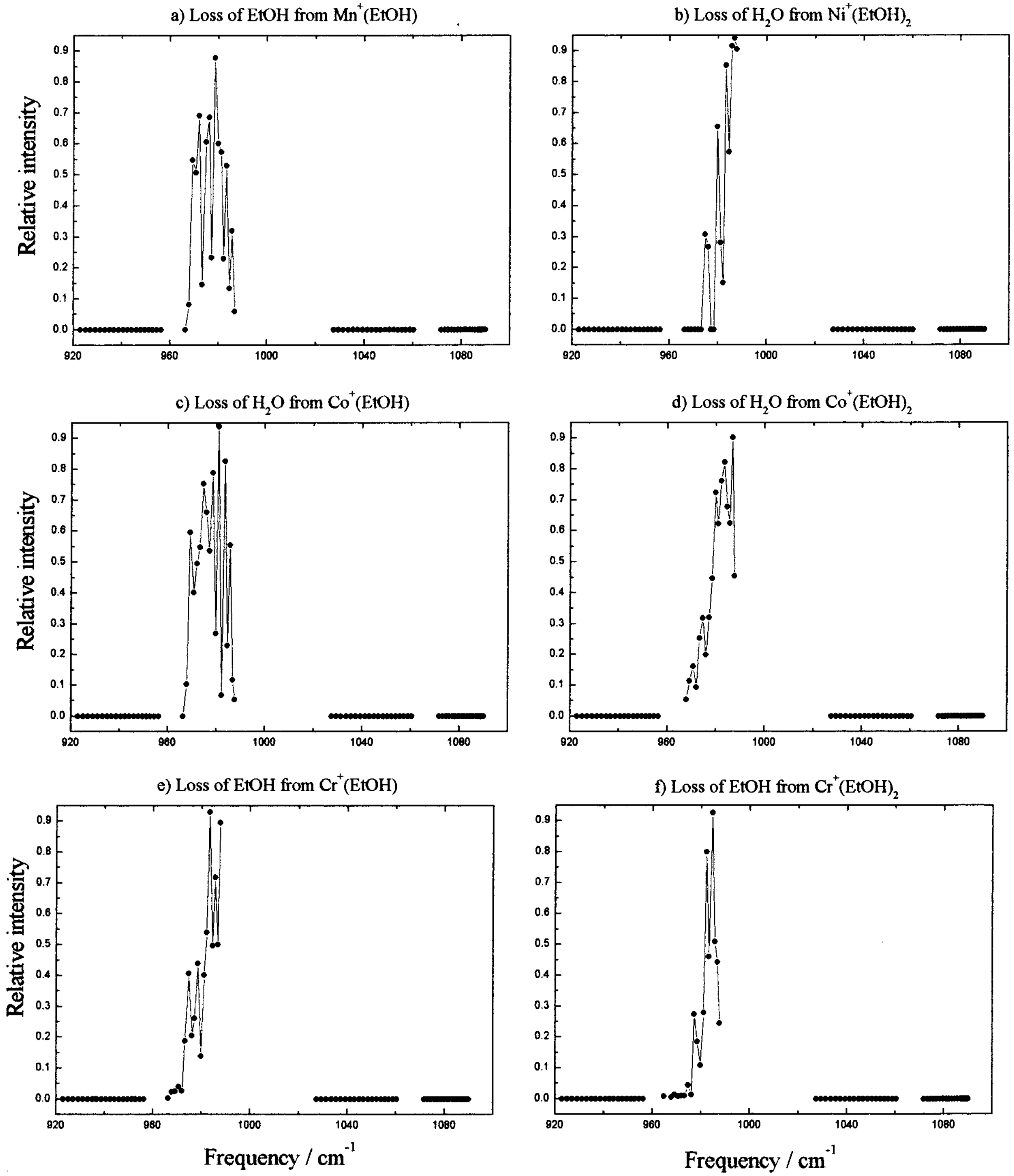

**Figure 5.** Photofragmentation patterns recorded for a range of $M^+$−ethanol complexes, where M is manganese, nickel, chromium, or cobalt. Each profile was recorded by measuring the photofragment yield as a function of $CO_2$ laser frequency.

by the presence of CO, but that it requires two molecules in the form of $Mn^+(CO)_2$ as opposed to a single molecule in $Fe^+CO$. Thus, for $Mn^+(CO)$ the exchange of CO for a single molecule of ethanol (the $Mn^+$ equivalent of reaction 3) probably leaves the metal ion in the ground electronic state [$^7S$ ($3d^5$ $4s^1$)], but with insufficient internal energy to react. Collision with a second ethanol molecule then promotes the formation of $Mn^+OEt(EtOH)$. From a consideration of Table 5, it would therefore appear that it is the presence of a 4s-electron on the $Fe^+$ and $Mn^+$ cations which drives the reaction leading to ethoxide formation and that, unlike $Fe^+(EtOH)$, $Mn^+(EtOH)$ contains $Mn^+$ in its ground state, which means that it cannot undergo the initial insertion step which leads to dehydration following infrared excitation.

A consideration of earlier work,[1,2] together with the results presented here, would imply that the promotion of a dehydration reaction requires the initial formation of an insertion complex or intermediate of the form $HO-M^+-C_2H_5$. There is a very strong parallel between the pattern of behavior seen here for $Fe^+$ ($^4F$, $3d^7$), $Ni^+$, and $Co^+$ and results recorded by Kickel and Armentrout following a study of the reaction of these cations with silane.[35] All three metals were assumed to react via an insertion intermediate, and in each case the requirements were that bonds to the metal were covalent and that the complex be

**Table 5.** Selected Electronic States of Transition Metal Cations[a]

| metal ion | ground state | excited states at 1 ≤eV | other states |
|---|---|---|---|
| Cr$^+$ | $^6$S (3d$^5$) | | $^6$D (3d$^4$ 4s$^1$) at 1.52 eV |
| | | | $^4$D (3d$^4$ 4s$^1$) at 2.42 eV |
| | | | $^4$G (3d$^5$) at 2.54 eV |
| Mn$^+$ | $^7$S (3d$^5$ 4s1) | | $^5$S (3d$^5$ 4s$^1$) at 1.17 eV |
| | | | $^5$D (3d$^6$) at 1.78 eV |
| Fe$^+$ | $^6$D (3d$^6$ 4s1) | $^4$F (3d$^7$) at 0.30 eV | $^4$D (3d$^6$ 4s$^1$) at 1.03 eV |
| | | | $^4$P (3d$^7$) at 1.68 eV |
| Co$^+$ | $^3$F (3d$^8$) | $^5$F (3d$^7$ 4s$^1$) at 0.52 eV | $^3$F (3d$^7$ 4s$^1$) at 1.29 eV |
| | | | $^1$D (3d$^8$) at 1.44 eV |
| | | | $^3$P (3d$^8$) at 1.65 eV |
| Ni$^+$ | $^2$D (3d$^9$) | | $^4$F (3d$^8$ 4s$^1$) at 1.16 eV |
| | | | $^2$F (3d$^8$ 4s$^1$) at 1.75 eV |

[a] Taken from ref 38.

in a low-spin state. The cation electronic states which met these requirements were Fe$^+$ ($^4$F, 3d$^7$), Co$^+$ ($^3$F, 3d$^8$), and Ni ($^2$D, 3d$^9$). We have already suggested that the excited state of Fe$^+$, ($^4$F, 3d$^7$), is probably responsible for the dehydration reaction because the electronic ground state appears to behave quite differently, and for the other two metals, Co$^+$ and Ni$^+$, Table 5 shows that the states concerned are in fact the electronic ground states.

Finally, we should address the situation regarding the chromium cation, and relevant to this discussion are the observations by Armentrout and Fisher on the state-dependent chemistry of Cr$^+$ with alkanes.[34] Ground-state Cr$^+$ has been shown to activate C−C bonds while excited quartet states will activate both C−C and C−H bonds. The selective activation of C−H bonds by the $^4$G state is attributed to a combination of the correct spin correlation with the required C−Cr$^+$−H intermediate and the presence of a vacant s-orbital.[34] Species which are covalently bonded to chromium cations have been shown to have quartet spin and, therefore, their formation from a sextet ground-state chromium cation would be forbidden. If it is again assumed that formation of an insertion complex leads to covalent bonding between the metal ion and the oxygen and carbon atoms, then this is unlikely to happen with Cr$^+$ in the ground $^6$D electronic state. Since the energies required to access the quartet states of Cr$^+$ are comparatively high (see Table 5) it is unlikely that they will be present in the ion trap, and therefore, the absence of a dehydration reaction from Cr$^+$(EtOH) can be understood. As with the other examples where there is no reactivity, the initial Cr$^+$−HOC$_2$H$_5$ complex will be held together by ion−dipole and induced dipole interactions, and it is this bond that breaks upon infrared photoexcitation.

## Conclusion

It has been shown that the combination of ion trap and tuneable laser radiation provides a way of probing details of the structures and reaction pathways of metal ion−molecule complexes. From these results on complexes containing ethanol, it has been possible to record the frequency dependencies of infrared absorption, and these data are used to comment on the initial structure of the M$^+$−alcohol complex. It has also been shown that photofragment yields are sensitive to isotopic substitution, and that the observed reaction pathways are sensitive to the electronic configuration of the metal ion.

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