Multiphoton ionization studies of C6H6–(CH3OH) n clusters. II. Intracluster ion–molecule reactions

Aaron W. Garrett and Timothy S. Zwier

Articles you may be interested in

Multiphoton ionization studies of C6H6–(CH3OH) n clusters. I. Comparisons with C6H6–(H2O) n clusters
J. Chem. Phys. 96, 7245 (1992); 10.1063/1.462429

Multiphoton ionization studies of clusters of immiscible liquids. II. C6H6–(H2O) n , n=3–8 and (C6H6)2–(H2O)1,2
J. Chem. Phys. 96, 3402 (1992); 10.1063/1.461941

Chemiluminescent ion–molecule reactions of O+ ions with CH4, C2H4, C2H6, C3H8
J. Chem. Phys. 71, 894 (1979); 10.1063/1.438392

Ion–molecule reaction mechanisms: Thermal energy gas phase reactions of 12C+ and 13C+ ions with CH4, C2H4, C2H6, C3H6, C3H8, and CD3CH2CD3
J. Chem. Phys. 65, 2574 (1976); 10.1063/1.433444

Ion–molecule reactions in the systems CF4–CH4 and CF4–C2H6
J. Chem. Phys. 62, 1027 (1975); 10.1063/1.430570

Multiphoton ionization studies of C_6H_6–$(CH_3OH)_n$ clusters. II. Intracluster ion–molecule reactions

Aaron W. Garrett and Timothy S. Zwier[a),b)]
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

The neutral C_6H_6–$(CH_3OH)_n$ clusters, which have been spectroscopically characterized in Paper I, serve here as precursors for the study of intracluster ion chemistry initiated by resonant two-photon ionization. Resonant enhancement allows ion chemistry product yields to be determined as a function of cluster size by selective excitation of a single size cluster with the laser. Most of the work presented here uses one-color resonant ionization via the 6_0^1 transition of the C_6H_6 chromophore in the cluster. No ion chemistry is observed for the 1:n clusters with $n \leqslant 2$. At $n = 3$, dissociative electron transfer (DET) to form $C_6H_6 + M_3^+$ (M = CH_3OH) is observed with a product yield of 6%. The remaining 94% of ionic products result from fragmentation of the 1:3 cluster by loss of a single CH_3OH molecule. The unprotonated M_3^+ product ion is unusual in that electron bombardment or photoionization of pure methanol clusters yields exclusively protonated methanol cluster ions. The attachment of a C_6H_6 molecule to the methanol cluster provides an extremely gentle photoionization mechanism which produces M_3^+ with little enough internal energy to preclude its breakup to $M_2H^+ + CH_2OH$ (or CH_3O). The opening of this product channel at $n = 3$ is consistent with estimates of the ionization potential of M_n clusters which predict an endothermic ET reaction at $n = 2$ which becomes exothermic at $n = 3$. Despite the increasingly exothermic DET and dissociative proton transfer product channels, larger clusters ($n \geqslant 4$) continue to predominantly undergo unreactive fragmentation. For the 1:4 and 1:5 clusters, in addition to DET products, dissociative proton transfer (DPT) products are also observed. The M_nH^+ product arises from proton transfer from $C_6H_6^+$, while $M_{n-1}H^+$ probably occurs by DPT within the M_n^+ cluster following loss of C_6H_6 in DET. Scans of the 1:2–1:5 clusters through their $6_0^1 1_0^1$ transitions yield a broader set of products which reflect the 5 kcal/mol increase in the reactant $(1:n)^+$ cluster internal energies.

I. INTRODUCTION

There is a great deal of effort currently being directed at developing and testing molecular-scale theories of solvent effects on chemical reactivity.[1,2] One area in which the solvent plays a particularly important role is in ion–molecule chemistry, where the interaction with the solvent is long range and strong. Recently, experimental techniques have been developed which provide a new perspective on ion–molecule reactivity and solvent effects on a molecular scale.[3,4] In these studies, unreactive neutral clusters containing two to tens of molecules are formed in a supersonic expansion and reaction is initiated by electron bombardment or photoionization of the cluster. In a few studies, resonance-enhanced multiphoton ionization has been used to selectively initiate ion–molecule chemistry in a single size cluster, allowing clear identification of reaction product ions with a given neutral cluster precursor.[3,5–8]

One theme which has begun to emerge from these studies is that cluster size plays an important role in determining the types and extent of ion–molecule reaction within the clusters. This is so largely because the energetic thresholds for various ion–molecule reaction channels vary over enormous ranges depending on the number and type of solvent molecule in the cluster. Less is known about the competition between different energetically open ion product channels and how they depend on cluster size and ion internal energy.

The present study presents an intriguing example of intracluster ion chemistry involving several reaction and fragmentation product channels occurring in competition with one another. The neutral precursor clusters used here are of the type C_6H_6–$(CH_3OH)_n$, where $n = 1$–5, building very directly on the spectroscopic studies of these clusters presented in Paper I.[9] We will see that following photoionization of the benzene molecule, a significant fraction of the ionic clusters containing three or more methanols undergo dissociative electron transfer (DET) to form $(CH_3OH)_n^+ + C_6H_6$. The exotic $(CH_3OH)_n^+$ product ion is not observed in the direct photoionization of neutral clusters, even at threshold, where protonated methanol clusters $H^+(CH_3OH)_n$ are produced exclusively.[10–13] The DET reaction occurs in competition with fragmentation and various dissociative proton transfer channels (DPT). Product branching ratios for these channels as a function of cluster size and ion internal energy are presented.
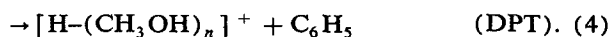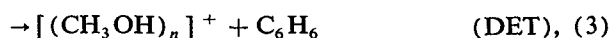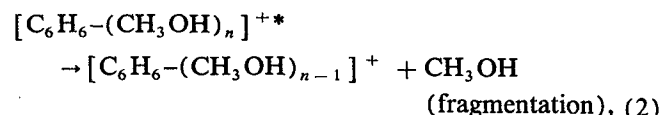
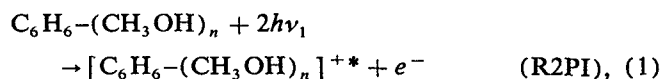[a)] Author to whom correspondence should be addressed.
[b)] Alfred P. Sloan Research Fellow.

II. EXPERIMENT

The molecular beam time-of-flight mass spectrometer (TOFMS) used in this study is identical to that in Paper I, to which the reader is referred. A given $C_6H_6-(CH_3OH)_n$ neutral cluster size is selected for photoionization using resonance enhancement through the S_0-S_1 transitions of the C_6H_6 chromophore in the cluster. Resonant two-photon ionization scans utilize the unfocused, doubled output of an excimer-pumped dye laser. Typical peak UV laser powers are 3×10^5 W/cm^2. Laser power studies indicate that the observed product ions result from two-photon processes. Relative product yields are determined from scans over the resonant features of the reactant complex while simultaneously monitoring ion signals from all relevant product mass channels using a 100 MHz digital oscilloscope.

III. RESULTS

In Paper I, we reported on the spectroscopy of neutral $C_6H_6-(CH_3OH)_n$ clusters. In that case, attention was focused on R2PI spectra taken monitoring unreactive ion mass channels $[C_6H_6-(CH_3OH)_n]^+$. Figures 1–3 present a series of scans over the same 6_0^1 region including scans monitoring mass channels which arise from intracluster ion–molecule chemistry. As is readily apparent from these spectra, resonant two-photon ionized $C_6H_6-(CH_3OH)_n$ clusters with $n \geqslant 3$ [Eq. (1)] react by dissociative electron transfer (DET) to form $(CH_3OH)_n^+$ [Eq. (3)], while those with $n \geqslant 4$ also undergo dissociative proton transfer (DPT) to form $H^+(CH_3OH)_n$ ions [Eq. (4)]. This intracluster ion chemistry is completely absent from the resonantly photoionized $C_6H_6-(H_2O)_n$ clusters[1,2] and from $C_6H_6-(CH_3OH)_n$ with $n \leqslant 2$ [Fig. 1(b)]. In all cases, the ion chemistry occurs in competition with fragmentation of the cluster [Eq. (2)] via loss of one (or sometimes two) methanol molecules.

$$C_6H_6-(CH_3OH)_n + 2h\nu_1$$

$$\rightarrow [C_6H_6-(CH_3OH)_n]^{+*} + e^- \quad \text{(R2PI)}, \quad (1)$$

$$[C_6H_6-(CH_3OH)_n]^{+*}$$

$$\rightarrow [C_6H_6-(CH_3OH)_{n-1}]^+ + CH_3OH$$

$$\text{(fragmentation)}, \quad (2)$$

$$\rightarrow [(CH_3OH)_n]^+ + C_6H_6 \quad \text{(DET)}, \quad (3)$$

$$\rightarrow [H-(CH_3OH)_n]^+ + C_6H_5 \quad \text{(DPT)}. \quad (4)$$

The dissociative electron transfer channel to form $[(CH_3OH)_n^+]$ is quite unexpected since only protonated methanol cluster ions are observed in either electron bombardment or photoionized pure methanol clusters.[10-13] While the resolution of our reflectron TOFMS is easily capable of distinguishing protonated from unprotonated clusters $(m/\Delta m \sim 1000)$, we have as an additional check carried out resonant two-photon ionization (R2PI) scans using CH_3OD which confirm that the major product is $[(CH_3OD)_n^+]$ and not $[(CH_3OD)_nD]^+$ or $[(CH_3OD)_nH]^+$.

Figures 4 and 5 present the relative product yields for the observed fragmentation, DET, and DPT channels fol-
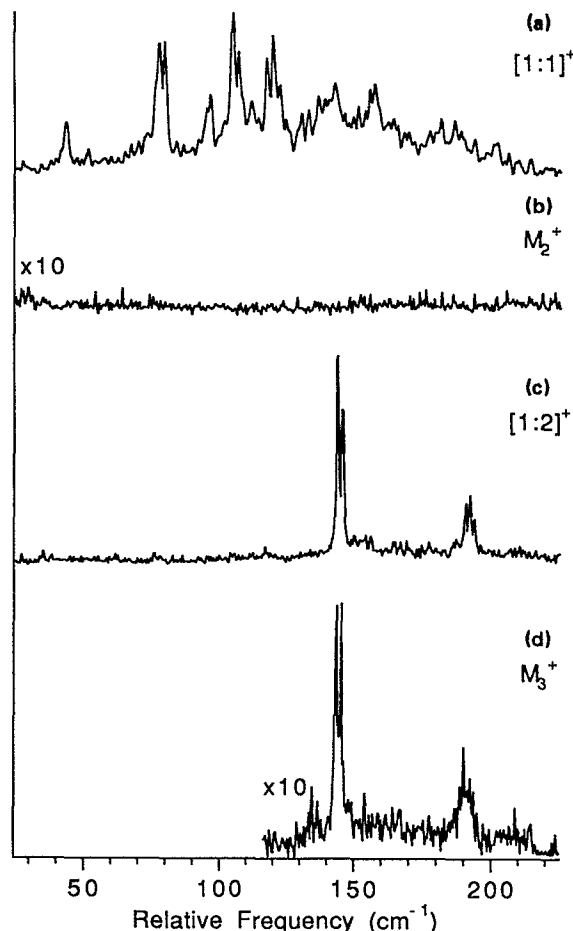

FIG. 1. R2PI scans in the 6_0^1 region of the $C_6H_6-(CH_3OH)_n$ clusters monitoring (a) $(1:1)^+$; (b) M_2^+ (M = methanol) at ten times higher sensitivity; (c) $(1:2)^+$, and (d) M_3^+ at ten times higher sensitivity. Note that no DET product is observed from the 1:1 and 1:2 clusters whose absorptions are shown in (a), while the 1:3 cluster, whose 6_0^1 transition is at 147 cm^{-1}, undergoes some DET reaction (d) in addition to the fragmentation into the 1:2 channel (c). Frequencies are given relative to the 6_0^1 transition of free C_6H_6.

lowing resonant ionization through the 6_0^1 and $6_0^1 1_0^1$ transitions of the 1:2, 1:3, 1:4, and 1:5 clusters. These yields are obtained by integrating the peak intensities of the 6_0^1 or $6_0^1 1_0^1$ ion signals in the relevant product channels in order to avoid nonresonant contributions from the signal. The measurements at $6_0^1 1_0^1$ increase the maximum internal energy in the cluster ion (determined by the photon energy) by 5.2 kcal/mol from those using the 6_0^1 transition as the intermediate state.

IV. DISCUSSION

One factor which plays a major role in determining the presence and efficiency of a given product channel is the energetic threshold for the channel relative to the internal energy of the photoionized reactant cluster. In photoionization, a distribution of ion internal energies is produced which reflect both direct ionization and autoionization processes in
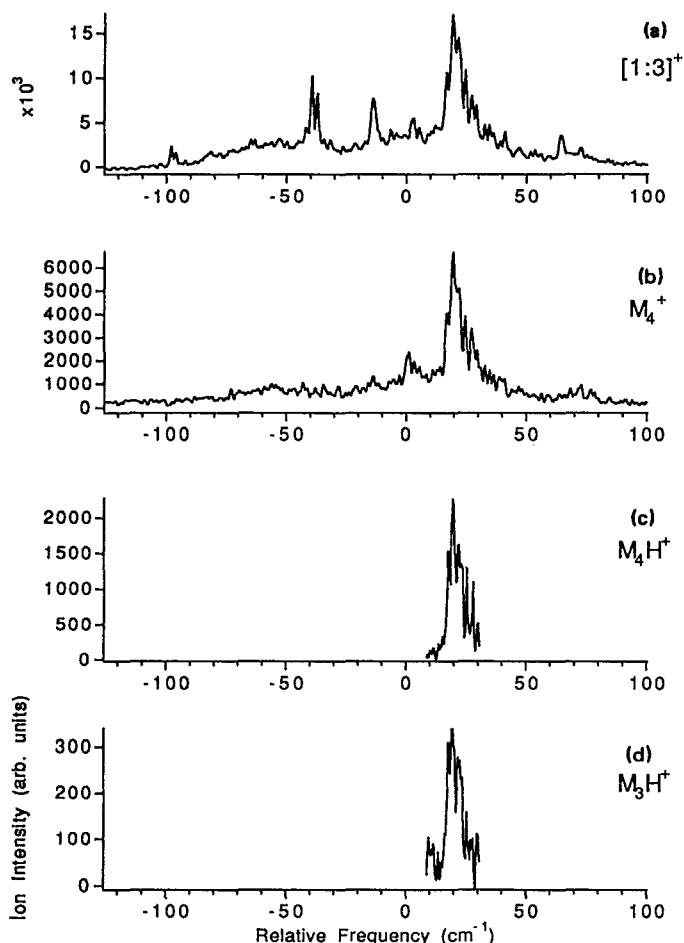
FIG. 2. The R2PI scan of the 6_0^1 transition of the 1:4 cluster (+ 19 cm^{-1}) monitoring (a) the (1:3)$^+$; (b) M_4^+; (c) M_4H^+; and (d) M_3H^+ mass channels.
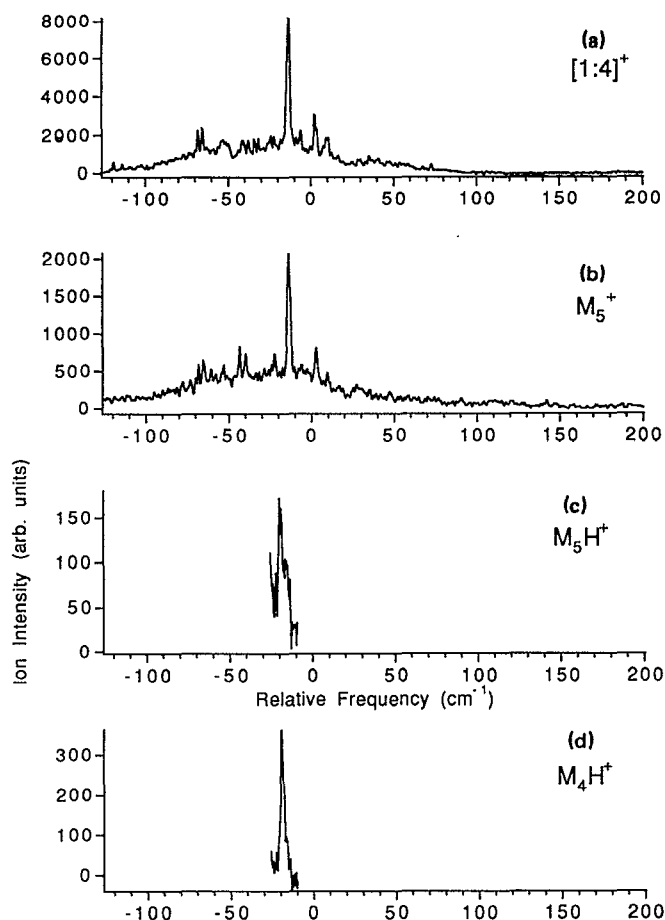
FIG. 3. The R2PI scan of the 6_0^1 transition of the 1:5 cluster (− 14 cm^{-1}) monitoring (a) the (1:4)$^+$; (b) M_5^+; (c) M_5H^+; and (d) M_4H^+ mass channels.

the cluster. In the free C_6H_6 molecule, R2PI through the 6_0^1 transition reaches 8 kcal/mol above the ionization threshold. In that case, the largely $\Delta v = 0$ Franck–Condon factors between the S_1 state of the neutral and the ground states of the ion result in the electron taking away most of the excess energy as kinetic energy.[14]

In clusters, on the other hand, the nature and strength of the intermolecular forces change significantly upon ionization, often leading to very different lowest-energy structures for the neutral and ionic clusters.[15–18] This is particularly true for the present clusters containing polar methanol molecules as solvent, where the good Franck–Condon factors between the S_1 state and the ion are to regions of the ionic potential energy surface far above the adiabatic ionization threshold for the cluster.[18–20] As we saw in Paper I, the efficient fragmentation of the photoionized clusters is one result of the high ion internal energies produced. Here, since the same photoionization process also initiates the intracluster ion chemistry, we expect to form a distribution of reactant cluster ion internal energies which favors ion internal energies near the maximum allowed by the photon energy.[20]

Figures 6–8 present energy level diagrams reflecting our best estimates of the energies of fragmentation, DET, and DPT product thresholds relative to the maximum ion energies produced by photoionization. Experimentally observed product channels are highlighted by placing them in boxes. In the figures, the zero of the energy level scales is taken to be the energy of the $C_6H_6^+$ + nCH_3OH asymptote. Table I collects the heats of formation of the relevant species. The thermochemistry of the protonated methanol clusters is known with good accuracy by virtue of several studies of these clusters.[21–23] The neutral cluster binding energies are not known from experiment. We estimate them using the calculations of Paper I after approximate correction for zero point energy effects.

An upper bound for the energy of the DET channel [Eq. (3)] on our relative scale is determined by the threshold for reaction (5)

$$C_6H_6^+ + nM \rightarrow M_{n-1}H^+ + CH_2OH + C_6H_6 \qquad (5)$$
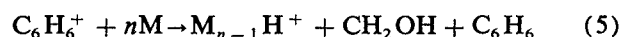
whose thermochemistry is determined by well-known heats of formation for all species.[23] If the CH_3O radical is formed instead of CH_2OH, the upper bound for DET would be 10 kcal/mol higher.[23] We assume that the observation of
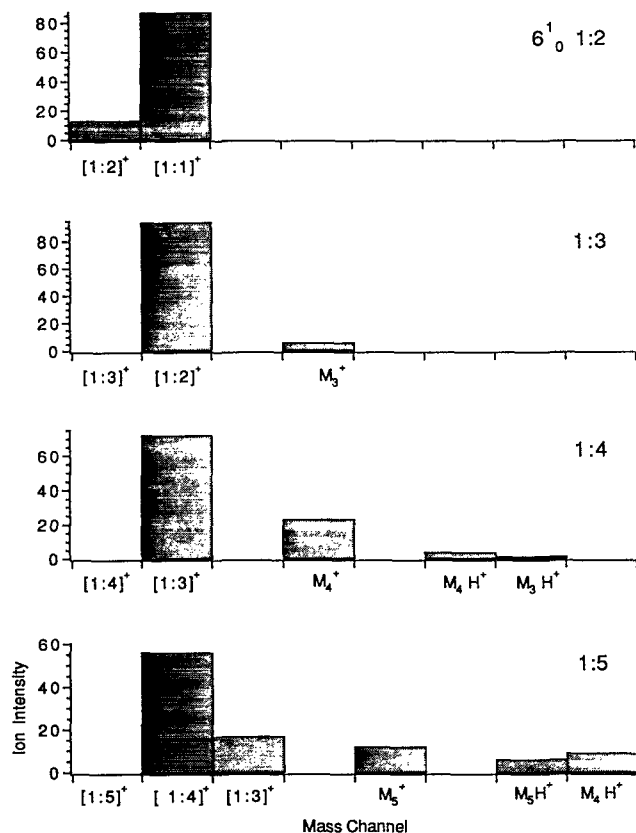
FIG. 4. Relative ion product yields for the 1:2–1:5 clusters photoionized via their respective 6_0^1 transitions. Product channels are separated into channels involving unreactive fragmentation, DET, and DPT.
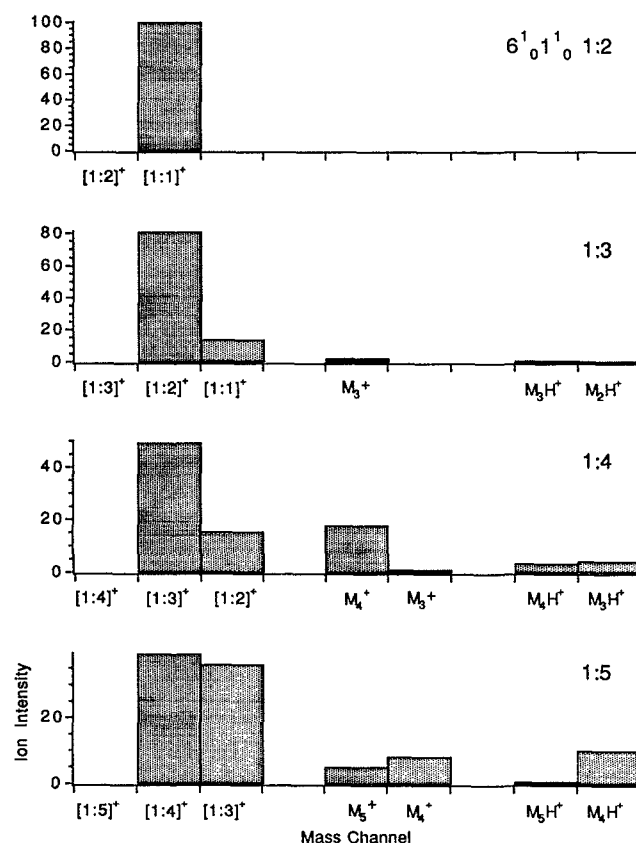

FIG. 5. Relative ion product yields for the 1:2–1:5 clusters photoionized via their respective $6_0^1 1_0^1$ transitions. The maximum ion internal energies are 5.2 kcal/mol above those in Fig. 4.

$[(CH_3OH)_n]^+$ ions in the present experiment arises because there is an energetic barrier to breakup of this ion to $M_{n-1}H^+ + CH_2OH$. The shaded region in the diagrams place some reasonable bounds on the height of such a barrier (0–10 kcal/mol) and thus loosely brackets the threshold for DET.

A. The 1:2 cluster

As Fig. 4 indicates, the only observed product channel in one-color R2PI of the 1:2 cluster is fragmentation via loss of a single CH_3OH to form $[C_6H_6-CH_3OH]^+$. Fragmentation is 86% $\pm$ 5% efficient using the 6^1 level of the S_1 state as the intermediate state and 80% $\pm$ 10% efficient at 0^0, despite our use of laser powers for which three-photon contributions to the ion signals are negligible.[15] The small change in the percentage of fragmentation accompanying the 3 kcal/mol increase in the two-photon energy confirms the notion that most of the cluster ions have an internal energy near the two-photon energy in Fig. 4, well in excess of the $(C_6H_6-CH_3OH)^+ + CH_3OH$ dissociation asymptote in both the 0^0 and 6^1 scans. Loss of CH_3OH from the ionic cluster occurs on a time scale fast compared to movement of the cluster ion in the ion source ($t < 1 \mu s$), since no asymmetry is observed in the arrival time profile of the parent or fragment. Fragmentation occurs almost exclusively by loss

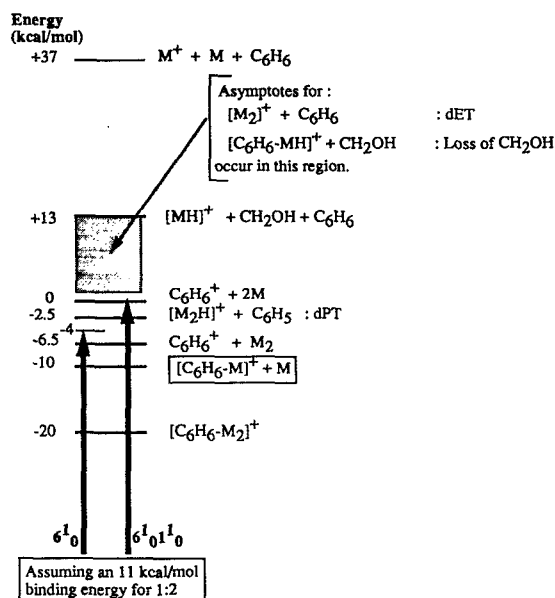**Ion-Molecule Chemistry in the 1:2 Cluster**

FIG. 6. An energy level diagram estimating thresholds for various intra-cluster ion–molecule reactions in the 1:2 cluster. Arrows indicate the maximum ion internal energies formed in R2PI scans using the 6_0^1 and $6_0^1 1_0^1$ transitions of the cluster. Observed channels are enclosed in boxes. Table I lists the thermochemical quantities used in making the figure.

Ion-Molecule Chemistry in the 1:3 Cluster

FIG. 7. An energy level diagram estimating thresholds for various intracluster ion–molecule reactions in the 1:3 cluster. Observed channels are enclosed in boxes.

of a methanol monomer rather than a methanol dimer, despite the fact that the latter channel should be accessible to many of the clusters. This favoring of evaporative loss of monomer units has been a trademark of cluster fragmentation in many types of clusters.[4]
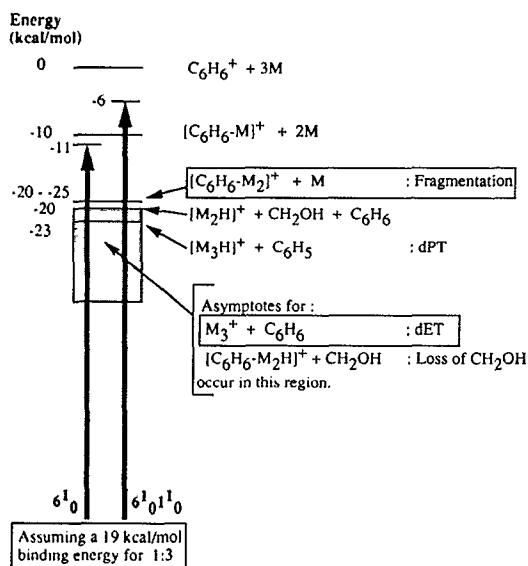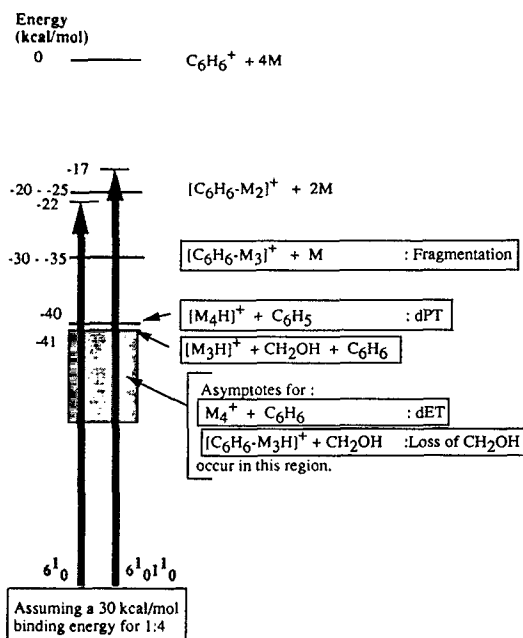
Ion-Molecule Chemistry in the 1:4 Cluster

FIG. 8. An energy level diagram estimating thresholds for various intracluster ion–molecule reactions in the 1:4 cluster. Observed channels are enclosed in boxes.

TABLE I. Thermochemical data relevant to the $[C_6H_6\text{-}(CH_3OH)_n]^+$ ion chemistry. The abbreviation CH$_3$OH = M is used at times.

Species	Heat of formation[a] (kcal/mol)	Proton affinity[b] (kcal/mol)	Binding energy D_e (D_0)[c] (kcal/mol)
H$^+$	+ 365.7		
C$_6$H$_6$	+ 19.8		
C$_6$H$_5$	+ 79	− 211	
C$_6$H$_6^+$	+ 233.2		
CH$_3$OH	− 48.2	− 182	
CH$_2$OH$_2^+$	+ 202.0		
CH$_2$OH	− 6.2		
CH$_3$O	+ 3.7		
M$_2$		− 211	7.6 (6.5)[e]
M$_3$		− 224	19.0 (14)[e]
M$_4$		− 231	32.7 (26)[e]
M$_2$H$^+$	55.3		
M$_3$H$^+$	− 13.9		
M$_4$H$^+$	− 78.2		
C$_6$H$_6$–M			5.8 (3.5)[e]
C$_6$H$_6$–M$_2$			13.5 (11)[e]
C$_6$H$_6$–M$_3$			23.8 (19)[e]
C$_6$H$_6$–M$_4$			37.5 (30)[e]
C$_6$H$_6^+$–M			∼10[d,e]
C$_6$H$_6^+$–M$_2$			∼20–25[d,e]
C$_6$H$_6^+$–M$_3$			∼30–35[d,e]

IP (C$_6$H$_6$) = 213 kcal/mol

Two-photon energy through 6_0^1 (221 kcal/mol)
Two-photon energy through $6_0^1 1_0^1$ (226 kcal/mol)

[a] Heats of formation of the unclustered species are taken from Ref. 23, the protonated methanol clusters from Ref. 21.
[b] Proton affinities are taken from Refs. 22 and 23.
[c] D_e binding energies are taken from Table III of Paper I. Zero point energy corrections are estimated to give the D_0 values in parentheses.
[d] These values are nothing more than reasonable guesses.
[e] These values are estimated quantities.

The lack of ion–molecule chemistry in the $[C_6H_6\text{-}(CH_3OH)_2]^+$ cluster appears to be a direct consequence of energetic constraints. Dissociative electron transfer, which is the dominating reaction channel in higher clusters, is predicted to be endothermic in R2PI through 6^1 (Fig. 6). This is the case because the ionization potential of CH$_3$OH is some 37 kcal/mol above that for C$_6$H$_6$ (Table I), so that even with the stabilization of CH$_3$OH$^+$ provided by a second methanol molecule, formation of $[(CH_3OH)_2]^+$ is still endothermic. Similarly, the high proton affinity of C$_6$H$_5$ (which clearly precludes proton transfer of C$_6$H$_6^+$ to CH$_3$OH) is nearly thermoneutral for transfer to (CH$_3$OH)$_2$ (see Table I and Fig. 6). Hence it is not surprising that no reaction products beside fragmentations are observed in the 1:2 clusters.
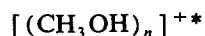
B. The 1:3 cluster

The $[C_6H_6\text{-}(CH_3OH)_3]^+$ cluster ion is the smallest sized 1:n cluster to undergo intracluster ion–molecule chemistry. The appearance of $[(CH_3OH)_3]^+$ (i.e., mass 96) is
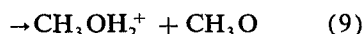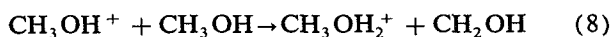
consistent with the energy level diagram of Fig. 7 which shows that the asymptote for DET is now well below the maximum ion internal energy produced in R2PI. Nevertheless, DET is still only a minor channel (6%) which competes only poorly with fragmentation via loss of CH_3OH (94%).

1. The formation of $[(CH_3OH)_3]^+$

The formation of a reaction product at mass 96 is notable for being exclusively the unprotonated methanol cluster ion. As mentioned earlier, when pure methanol clusters are either electron bombardment or photoionized,[10–13] only protonated cluster ions are observed due to exothermic ion–molecule reactions of the type

$$[(CH_3OH)_n]^{+*}$$

$$\rightarrow [(CH_3OH_2)^+ - (CH_3OH)_{n-2}] + CH_2OH \quad (6)$$

$$\rightarrow [(CH_3OH_2)^+ - (CH_3OH)_{n-2}] + CH_3O. \quad (7)$$

The bimolecular analogs of these reactions

$$CH_3OH^+ + CH_3OH \rightarrow CH_3OH_2^+ + CH_2OH \quad (8)$$

$$\rightarrow CH_3OH_2^+ + CH_3O \quad (9)$$

are exothermic by 24 and 14 kcal/mol, respectively.[16–18] Both these facts suggest that the initially unprotonated cluster ions would be inherently unstable with respect to loss of CH_2OH or CH_3O. However, in recent experiments by Vaidyanathan et al.,[13] electron bombardment ionization of Ar/CH_3OH heteroclusters has successfully produced significant quantities of unprotonated $[Ar_m(CH_3OH)_n]^+$ ions via intracluster Penning ionization involving high-lying states of the argon neutrals. The present study offers a second example of the formation of unprotonated methanol cluster ions, this time mediated by C_6H_6. The attachment of the methanol clusters to a C_6H_6 chromophore offers an extremely gentle means of producing unprotonated M_n^+ clusters by photoionizing the cluster with only 9.60 eV energy via the C_6H_6 chromophore. In the case of the 1:3 cluster, the unprotonated M_3^+ products can be formed completely free from interference from protonated clusters. This mechanism thus provides a route producing the novel M_n^+ cluster ions for subsequent spectroscopic and mass spectrometric study.

The formation of the DET product M_3^+ (M = methanol) provides supporting evidence for the neutral C_6H_6–M_3 cluster possessing a structure composed of hydrogen-bonded methanols all attached to the same side of the benzene ring (Paper I). It seems unlikely that DET to form M_3^+ would occur from an initial geometry in which methanol molecules are on both sides of the benzene ring rather than as an aggregate on the same side.

The structure of the mass 96 ion is not determined in the present work. However, it seems likely that the M_3^+ cluster exists either as $[CH_3OH_2^+ - CH_2OH - CH_3OH]$ or as $[CH_2OH_2^+ - (CH_3OH)_2]$ in which proton transfer within the methanol cluster has occurred with cluster energy insufficient to allow its breakup to form the protonated M_2H^+ ion. Loss of the C_6H_6 molecule from the cluster provides the means by which the M_3^+ ion is stabilized below its

$M_2H^+ + CH_2OH/CH_3O$ dissociation asymptote.

The only energetically allowed channel which competes successfully with DET is fragmentation to form $(C_6H_6–M_2)^+ + M$, which dominates the product distribution (94%). No parent 1:3 cluster ions are observed in our experiment. Thus the observed processes are the following:

$$(C_6H_6–M_3)^{+*} \rightarrow (C_6H_6–M_2)^+ + M, \quad k_{frag}(E) \quad (10)$$

$$\rightarrow M_3^+ + C_6H_6, \quad k_{DET}(E). \quad (11)$$
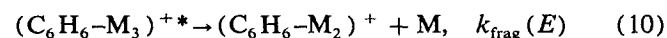
One could imagine two limiting cases for the competition between DET and fragmentation. In one limit, the energy dependence of the rate constants is either small enough or similar enough in the two channels that the observed product distribution directly reflects the relative magnitudes of the rate constants for fragmentation and DET; i.e., the product yields are kinetically controlled. In this case, the rate of fragmentation would provide an "internal clock" for the DET reaction if it could be determined by other means.

In the second limit, the observed product distribution will reflect energetic constraints rather than kinetics. This would occur if $k_{frag}(E)$ is much greater than $k_{DET}(E)$ for energies where fragmentation can occur. Then all cluster ions with internal energies above the fragmentation threshold would undergo fragmentation, while the remaining, lower energy cluster ions would react via DET. More complete control over the ion internal energies produced or detected (e.g., via photoelectron–photoion coincidence measurements)[18,19] will be required before the energy dependences of the reaction rates can be determined unambiguously.

2. Reactions which are not observed

The formation of unprotonated M_3^+ ions is unusual in a second respect—it occurs to the exclusion of several other energetically open channels, most notably those involving dissociative proton transfer [Eq. (4)]. Careful searches for the DPT products M_3H^+ ($+ C_6H_5$) and M_2H^+ ($+ CH_2OH + C_6H_6$), or the CH_2OH loss channel to produce $C_6H_6–M_2H^+$ place upper bounds on these channels at less than 1% of the 1:2 fragment channel (Fig. 4), nearly ten times less than the observed yield of DET products.

Again, energetics could play a significant role in suppressing the proton transfer channels if the rate constants for the product channels were sensitively dependent on their exothermicity. Then DET, if it is more exothermic than the proton transfer channel, might be favored on that basis. However, we would expect this argument to hold less weight in larger clusters where the exothermicities of all reaction channels are significantly greater, yet proton transfer channels remain small (Fig. 4).

The preference of the $[C_6H_6–(CH_3OH)_3]^+$ cluster for DET may result from its reaction trajectories starting from a neutral precursor cluster structure which favors DET over DPT. The photoionization scheme employed (via resonant excitation of the C_6H_6 molecule) is to regions of the ionic potential energy surface which initially differ little in geometry from those of the neutral cluster with the positive charge initially residing on the C_6H_6 molecule. The $(C_6H_6–M_3)^+$ reactant ion, with its large internal energy,

will likely be liquid-like in its subsequent behavior, with the methanol solvent molecules reorienting their dipoles to the newly formed charge on benzene. Nevertheless, the transfer of a proton or hydrogen atom from $C_6H_6^+$ to M_3 may be inhibited by the large distance from their in-plane positions in $C_6H_6^+$ to what is initially an out-of-plane methanol trimer. In addition, the nuclear reorganization required to accept this proton or hydrogen atom into a low energy configuration (i.e., trapped between three methanol molecules) may be significant. Both these factors would inhibit DPT. On the other hand, the close proximity and significant interaction of the methanol trimer with the benzene π cloud should facilitate electron transfer, which is often facile even at large intermolecular separations.[24]

C. The 1:4 cluster

The 1:4 cluster exhibits a more diverse intracluster ion chemistry than did the 1:3 cluster. Once again, no parent ions are observed, with fragmentation via loss of a single methanol still dominating the product distribution (72%). However, the M_4^+ DET product now competes much more effectively with fragmentation, accounting for 22% of the observed products. Aside from this increase in DET efficiency, the most notable change in the 1:4 cluster is the appearance of two DPT products M_3H^+ ($\sim$1%–2%) and M_4H^+ ($\sim$4%).

The energy level diagram of Fig. 8 indicates that asymptotes for all observed channels are now well below the maximum ion internal energy formed in R2PI. Furthermore, the preponderance of fragmentation products confirms that the majority of the $(1:4)^+$ clusters are born in photoionization with internal energies far in excess ($>$ 10 kcal/mol) of that required to react. Despite this, the product distribution is highly nonstatistical, favoring the *high energy* fragmentation product over DET and DPT product channels which possess thresholds at least 10 kcal/mol lower in energy.

Fragmentation also serves to shut off DET in the fragment clusters. This is borne out by the lack of M_3^+ products which could result if DET were to occur following loss of methanol. The loss of internal energy which accompanies fragmentation of CH_3OH must form the 1:3 cluster ion with insufficient energy to undergo DET subsequent to fragmentation.

The weak appearance of the M_4H^+ and M_3H^+ DPT product ions (Fig. 4) indicates that the lowering of the DPT product thresholds which occurs upon addition of a fourth methanol molecule enhances the rate of the proton transfer reaction relative to other channels. In spite of this, DET still is much preferred over DPT in R2PI through the 6^1 level. In fact, given the propensity of the 1:4 cluster to undergo DET, it seems likely that the actual mechanism of DPT involves electron transfer to form M_4^+–C_6H_6 followed by hydrogen atom transfer from C_6H_6 to M_4^+. If this is true, the M_4^+–C_6H_6 species plays a central role in the intracluster reaction dynamics. The observed product yields then reflect the competition between loss of C_6H_6 and H-atom transfer in M_4^+–C_6H_6.
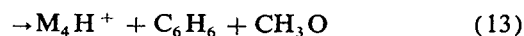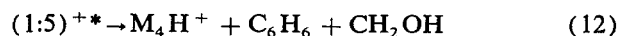
While it may be little more than coincidence, it is interesting to note that the DPT channel first appears in the 1:4 cluster whose structure is predicted by the calculations of Paper I to incorporate a cyclic methanol cluster curling around on the side of the benzene ring. This structure, which is initially accessed in the photoionization process, seems to be poised to undergo proton or hydrogen atom transfer in a way that the out-of-plane, chain-type methanol trimer was not.

D. The 1:5 cluster

Because of the accumulating errors in our estimates of energy thresholds for the various reaction channels, we have chosen not to present a detailed energy level diagram specific to the 1:5 cluster. Nevertheless, the trend which is observed in the 1:2–1:4 clusters toward increased exothermicity of the reaction channels with increasing cluster size should continue in the 1:5 cluster. It is somewhat surprising, then, that despite the increased exothermicity, the relative fraction of reactant cluster ions which undergo reaction is still only about one-third the size of the unreactive fragmentation channels (Fig. 4). It appears that any increase in the rates of the DET and DPT reactions which may accompany this increased exothermicity is offset by similar increases in the rate of fragmentation.

One clear change in the product distribution of the 1:5 cluster ion is the presence of the $(1:3)^+$ product arising from loss of two methanols. The absence of the corresponding channel in smaller clusters points to the 1:5 cluster overcoming an energetic threshold for loss of two methanols. In the 1:4 cluster (Fig. 8), the maximum internal energy produced in R2PI is near the threshold for loss of two methanol monomers. By analogy, then, it appears that the threshold which is overcome in the 1:5 cluster is one involving the loss of two monomers rather than the lower energy threshold for loss of a methanol dimer from the cluster. The preference for evaporative loss of monomer units from ionic clusters has been seen in several previous studies.[25]

In terms of the ion–molecule chemistry, the most important change in the 1:5 cluster is an increase in the number of DPT products at the expense of DET products. The majority of the increase is observed in the M_4H^+ channel. This channel can arise from at least three distinct pathways, which we cannot distinguish at present

$$(1:5)^{+*} \rightarrow M_4H^+ + C_6H_6 + CH_2OH \qquad (12)$$

$$\rightarrow M_4H^+ + C_6H_6 + CH_3O \qquad (13)$$

$$\rightarrow M_4H^+ + C_6H_5 + CH_3OH. \qquad (14)$$

However, the first two channels offer the most likely explanation. The higher internal energies of the photoionized $(1:5)^+$ cluster allow DPT to occur within the M_5^+ ions produced in DET, thereby producing $M_4H^+ + CH_2OH$ (or CH_3O).

E. Ion internal energy and product yields

The results of Fig. 5 provide an opportunity to evaluate, at least in a general way, the effect of increasing cluster ion

internal energy on the intracluster reaction product yields. The figure summarizes the product yields obtained using the 6^11^1 level of the neutral clusters as the intermediate state in one-color R2PI. Since ν_1 has a vibrational frequency of 923 cm^{-1} in the excited state, the maximum ion internal energy produced in this excitation scheme is ~ 1840 cm^{-1} (5.2 kcal/mol) above that in the scans using the 6^1 level as the intermediate state. In using the 6^11^1 level as intermediate, the possibility of vibrational predissociation in the neutral cluster must be taken into account. Such predissociation can occur if the binding energies in the neutral excited state clusters are less than 1440 cm^{-1} (4.1 kcal/mol) and if predissociation is fast compared to ionization from the S_1 state. However, based on previous experience with related C_6H_6–X_n clusters, it seems unlikely that this is the case. First, the lowest energy dissociation channel predicted by calculations involves fragmentation to $C_6H_6 + M_n$, but even this channel is calculated to be significantly endothermic for $n = 3$–5 (Table III of Paper I). Second, since the weakest bond in the neutral is between C_6H_6 and $(CH_3OH)_n$, the ion intensity should transfer to the $C_6H_6^+$ mass channel if predissociation in the S_1 state is occurring. This is not observed.

The second set of arrows in the energy level diagrams of Figs. 6–8 shows the maximum ion internal energies which are reached in the R2PI scans through the $6_0^1 1_0^1$ transitions of the clusters. A comparison of the product yields of Fig. 4 (6_0^1) and Fig. 5 ($6_0^1 1_0^1$) highlights the following changes:

First, photoionization of 1:n clusters through the 6^11^1 intermediate state produces significant increases in the extent of fragmentation in the cluster ions. This is seen most readily in the unreactive fragmentation channels where the 1:$(n-2)$ product channel is formed in much higher intensities than at the lower photon energy. It thus appears that the increased photon energy is resulting, as expected, in increased cluster ion internal energies skewed toward the maximum internal energy which can be produced in the R2PI process.

Second, in the 1:3 and 1:4 clusters, the 1:$(n-2)$ channel was not observed at all at 6^1, but makes up about 20% of the products at 6^11^1. This likely indicates that the 5 kcal/mol additional internal energy overcomes an energetic threshold to the loss of two methanol molecules. The energy level diagrams of Figs. 6–8 support this view. While the fragmentation process involving the loss of two methanol monomers is estimated to be right near threshold at 6^1, it becomes clearly energetically allowed at 6^11^1.

Third, the $6_0^1 1_0^1$ scan over the 1:3 resonance shows a small, but real presence of DPT products which was completely absent from the 6_0^1 scans. In this case, the threshold for DPT is already well below the maximum ion internal energy produced in R2PI (Fig. 6). However, the tunneling mechanism which probably operates in the DPT would exhibit a rate of DPT which is a sensitive function of the internal energy of the cluster, consistent with the observed turn on of this product channel with a modest change in reactant cluster energy.

Fourth, there is a marked increase in the $M_{n-1}H^+$ pro-

ton transfer product channels in the 1:4 and 1:5 clusters. As we noted previously, it seems likely that the $M_{n-1}H^+$ product is produced by DET to form $M_n^+ + C_6H_6$ followed by loss of CH_2OH or CH_3O from the M_n^+ cluster. The increased energy content of the cluster favors such double fragmentation channels, highlighting the small energy regime over which M_n^+ cluster ions can be produced without subsequent intracluster DPT to form $M_{n-1}H^+$ clusters.

Fifth, while not shown in Fig. 5, we do have limited evidence for formation of yet another product; namely, the 1:$M_{n-1}H^+$ clusters formed by loss of CH_2OH or CH_3O. This product channel is obscured by unprotonated ^{13}C-containing clusters of the same mass, making quantitative assessments uncertain. The lower energy scans using the 6^1 level show intensities near enough to the expected ^{13}C natural abundance that products from ion chemistry cannot be clearly identified. However, at 6^11^1, the resonant intensities in the larger clusters are well above natural abundance (e.g., 26%; cf. 10% natural abundance for the 1:4 cluster), indicating that a small fraction of the energized reactant cluster ions do fragment by loss of CH_2OH or CH_3O. Further work with CD_3OH and CH_3OD is needed to determine the extent and mechanism of this reaction channel more carefully.

Finally, it should be noted that in each of the reactive clusters (1:3, 1:4, and 1:5), roughly the same total percentages of each class of reaction (fragmentation, DET, and DPT) are produced at higher energy (Fig. 5) as at lower energy (Fig. 4). For example, in the 1:4 cluster, fragmentation channels account for 72%/71%, DET for 22%/20%, and DPT for 5.5/9% in R2PI scans through $6^1/6^11^1$. This occurs despite the significant changes noted earlier in the *distribution of products* within each type of reaction. One possible interpretation of this result is that most of the reaction trajectories taken by the cluster tend to split early in their trajectories into groups which can be categorized as unreactive fragmentation, DET, or DPT. The extent of fragmentation within a given reaction type would then be determined by the internal energy of the cluster initially produced.

V. CONCLUSIONS

Resonant two-photon ionization of C_6H_6–$(CH_3OH)_n$ clusters has been used to initiate a rich array of intracluster ion–molecule reactions. Energetics play an important role in the cluster size dependence of the ion chemistry. While the ionization potential of an isolated CH_3OH is 37 kcal/mol above that of C_6H_6, $(CH_3OH)_n$ clusters with $n \geqslant 3$ have ionization potentials below that of C_6H_6 by virtue of the stabilization provided by strong charge/dipole interactions. In keeping with this predicted energetics, the smallest sized cluster observed to undergo ion chemistry is the 1:3 cluster. At low cluster internal energies, the $(1:3)^+$ cluster reacts exclusively via dissociative electron transfer to form the $(CH_3OH)_3^+$ ion. The unusually gentle ionization mechanism provided by resonant ionization through C_6H_6 allows this otherwise unstable ion to be stabilized free from the production of protonated methanol clusters.

As the cluster size continues to increase, so does the

number of distinct product channels. In addition to the major DET channel, higher clusters also undergo minor amounts of DPT and (probably) formation of C_6H_6–M_nH^+ ions by loss of CH_2OH. The slow rate of DPT is not unexpected given the weak acidity of $C_6H_6^+$ (Table I). Nevertheless, even when the DPT channel is strongly exothermic, DET seems to compete favorably with DPT. We propose a mechanism for DPT which involves electron transfer followed by hydrogen atom transfer from C_6H_6 to $(CH_3OH)_n^+$.

Several avenues for further work are suggested. One involves further characterization of the unprotonated methanol cluster ions by either collision-induced dissociation or photodissociation. Two-color R2PI scans would allow an exploration of a larger range of cluster ion internal energies than was possible in this study. The photoelectron kinetic energy distribution can be used to more firmly pin down the internal energies of the reactant cluster ions. Finally, the mechanisms of the minor reaction channels can be examined in further detail by experiments using CH_3OD, CD_3OH, and C_6D_6.

ACKNOWLEDGMENTS

[1] J. T. Hynes, in *Theory of Chemical Reaction Dynamics*, edited by M. Bauer (Chemical Rubber, Boca Raton, 1985), Vol. 4, p. 171.

[2] P. Nanngi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).

[3] B. Brutschy, J. Phys. Chem. **94**, 8637 (1990).

[4] A. W. Castleman, Jr. and R. G. Keesee, Chem. Rev. **86**, 589 (1986), and references therein.

[5] B. Brutschy, J. Eggert, C. Janes, and H. Baumgartel, J. Phys. Chem. **95**, 5041 (1991), and references therein.

[6] T. Maeyama and N. Mikami, J. Phys. Chem. **94**, 6973 (1990).

[7] J. J. Breen, W. B. Tzeng, K. Kilgore, R. G. Keesee, and A. W. Castleman, J. Chem. Phys. **90**, 19 (1989).

[8] J. Syage, J. Phys. Chem. **93**, 170 (1989).

[9] A. W. Garrett and T. S. Zwier, J. Chem. Phys. **96**, 7245 (1992).

[10] Y. Mori and T. Kitagawa, Chem. Phys. Lett. **128**, 383 (1986).

[11] K. D. Cook, G. G. Jones, and J. W. Taylor, Int. J. Mass Spectrosc. Ion Phys. **35**, 273 (1980).

[12] A. W. Castleman, W. B. Tzeng, S. Wei, and S. Morgan, J. Chem. Soc. Faraday Trans. **86**, 2417 (1990); S. Morgan, R. G. Keesee, and A. W. Castleman, J. Am. Chem. Soc. **111**, 3841 (1989); S. Morgan and A. W. Castleman, J. Phys. Chem. **93**, 4544 (1989); J. Am. Chem. Soc. **109**, 2867 (1987).

[13] G. Vaidyanathan, M. T. Coolbaugh, W. R. Peifer, and J. F. Garvey, J. Chem. Phys. **94**, 1850 (1991).

[14] S. R. Long, J. T. Meek, and J. P. Reilly, J. Chem. Phys. **79**, 3206 (1983).

[15] R. I. McKay, E. J. Bieske, I. M. Atkinson, F. R. Bennett, A. J. Bradley, M. W. Rainbird, A. B. Rock, A. S. Uichanco, and A. E. W. Knight, Aust. J. Phys. **43**, 683 (1990); E. J. Bieske, R. I. McKay, F. R. Bennett, and A. E. W. Knight, J. Chem. Phys. **92**, 4620 (1990).

[16] G. Reiser, O. Dopfer, R. Lindner, G. Henri, K. Müller-Dethlefs, E. W. Schlag, and S. D. Colson, Chem. Phys. Lett. **181**, 1 (1991).

[17] C. Y. Ng, Adv. Chem. Phys. **52**, 263 (1983).

[18] S. Tomoda and K. Kimura, in *Vacuum Ultraviolet Photoionization and Photodissociation of Molecules and Clusters*, edited by C. Y. Ng (World Scientific, Singapore, 1991).

[19] K. Norwood, A. Ali, and C. Y. Ng, J. Chem. Phys. **95**, 8029 (1991).

[20] J. R. Gord, A. W. Garrett, R. E. Bandy, and T. S. Zwier, Chem. Phys. Lett. **171**, 443 (1990); A. J. Gotch and T. S. Zwier, J. Chem. Phys. **93**, 6977 (1990).

[21] S. T. Graul and R. R. Squires, Int. J. Mass Spectrosc. Ion Proc. **81**, 183 (1987).

[22] R. Knochenmuss, O. Cheshnovsky, and S. Leutwyler, Chem. Phys. Lett. **144**, 317 (1988).

[23] *Gas Phase Ion and Neutral Thermochemistry*, edited by S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, J. Phys. Chem. Ref. Data **17**, 231 (1988).

[24] N. S. Hush, Coord. Chem. Rev. **64**, 135 (1985).

[25] See, e.g., A. W. Castleman, W. B. Tzeng, S. Wei, and S. Morgan, J. Chem. Soc. Faraday Trans. **86**, 2417 (1990).