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6. AUTHOR(S)

James Stry, M. Todd Coolbaugh, Edward Turos, and James F. Garvey

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Dept. of Chemistry, Acheson Hall
State University of New York at Buffalo
Buffalo, NY
14214

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Novel Gas Phase Ion Molecule Reactions of C_{60}^{++} with O_2 and NH_3

by

James Stry, M. Todd Coolbaugh, Edward Turos, and James F. Garvey*

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Acheson Hall
Department of Chemistry
University at Buffalo
The State University of New York at Buffalo
Buffalo, NY
14214

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Novel Ion-Molecule Reactions of C_{60}^{++} with O_2 and NH_3

James J. Stry, M. Todd Coolbaugh
Edward Turos, and James F. Garvey*,†

Acheson Hall,
Department of Chemistry,
State University of New York at Buffalo,
Buffalo, New York
14214

Abstract

We have recently utilized a tandem triple quadrupole mass spectrometer to probe the gas phase ion-molecule chemistry of C_{60}^{++} with a variety of target gases, at low collision energies. We have observed a high degree of reactivity of C_{60}^{++} with oxygen to produce C_{60}^{+}, $C_{60}O^{2+}$ and $C_{60}O^{+}$. Likewise, we have also observed reactivity of C_{60}^{++} with ammonia to produce $C_{60}NH_2^{+}$, $C_{60}NH_2(NH_3)^{+}$, $C_{60}NH_2(NH_3)_2^{+}$ and $C_{60}NH_2(NH_3)_3^{+}$. We propose that the product ions result from an electron transfer reaction followed by covalent bond formation. All reactions were observed to be highly dependent on collision energy (0.1-0.3 eV) and target gas pressure (1.2-10 mtorr). We believe that these processes are part of a larger family of charge exchange reactions for C_{60}^{++}, which occur for any molecule whose ionization potential lies below 12.25 eV, the first ionization potential of C_{60}^{+}.

With the recent discovery of a new class of carbon molecules, named fullerenes[1-3], a new area of chemical endeavor has been opened. Since Kratschmer and coworkers[4] have shown that C_{60} can be obtained in relatively large amounts by pyrolyzing graphite in a helium environment, an intense study of the physical and chemical properties of this intriguing class of carbon molecules has begun. In addition, a wide range of theoretical[5-8] calculations have been carried out.

The solution phase chemistry of C_{60} with oxygen[9] and various amines[10] has shown some insight into its unique reactivity. Cox and coworkers[9] have reported the production and isolation of a fullerene mono epoxide, $C_{60}O$, produced by dissolving C_{60} in oxygen rich benzene. C_{60}, when dissolved in propylamines[10], undergoes addition of as many as twelve solvent molecules to the C_{60} framework. A stepwise mechanism has been proposed for this involving electron transfer from the amine to C_{60} followed by covalent bond formation between the resulting ions. This reactivity of C_{60}, along with its large electron affinity (2.6 -2.8 eV[11]), strongly suggests that it can behave as a good electrophile[10] in reactions with heteronucleophiles.

In this communication we report the gas-phase associative charge transfer reactions of C_{60}^{++} with the neutral molecules NH_3, ND_3, and O_2. All experiments reported in this study were performed on a tandem triple quadrupole mass spectrometer (VG20-250). The fullerene extract (obtained by extracting fullerene rich soot, provided by the Texas Fullerene Corporation, with toluene)[12] was introduced into the ion source of the mass spectrometer via a heated solid probe inlet ($570^{o}C$). Following electron impact ionization (70 eV electron impact energy), the first quadrupole is employed to mass select the C_{60}^{++} cation (i.e., the mass window employed was 355-365 m/z). These ions were then directed, via a second quadrupole filter, into a collision cell containing neutral molecules of either NH_3 (Linde, anhydrous grade), ND_3 (Isotec, 99.1 atom percent deuterium) or O_2 (Airco, 99.6%) at pressures ranging from 0.1 to 10 mtorr. The third quadrupole filter was mass scanned to analyze the ions exiting the collision cell, including any new species that had been produced via ion-molecule reactions occurring within the cell.

Doubly charged fullerene cations were observed to react with each of these neutral target molecules while the singly charged fullerene cations showed no reactivity. Thus, the passage of C_{60}^{++} through 2-10 mtorr of oxygen at collision energies of 0.01-0.5 eV (E_{cm}) produced the ions: $C_{60}O^{2+}$ *(368 amu)*, C_{60}^{+} *(720 amu)*, $C_{60}O^{+}$ *(736 amu)*, as well as unreacted C_{60}^{++}*(360 amu)*. The most abundant product ion was $C_{60}O^{+}$ while the $C_{60}O^{2+}$ and C_{60}^{+} ions were observed at very low intensities. We note that the $C_{60}O_2^{++}$ ion is not observed under any conditions.

The identification by Cox and coworkers[9] of $C_{60}O$ (obtained in solution) as an epoxide encourages us to believe that we are producing the ionized form ($C_{60}O^{+}$) of this epoxide. A possible mechanism for this oxygenation reaction is as follows (the ions which we directly observe are shown in bold face):

$$\mathbf{C_{60}^{++}} + O_2 \longrightarrow \{C_{60} - O_2\}^{++} \quad (1)$$

$$\{C_{60} - O_2\}^{++} \longrightarrow \mathbf{C_{60}O^{++}} + O \quad (2a)$$

$$\longrightarrow \mathbf{C_{60}O^{+}} + \mathbf{O^{+}} \quad (2b)$$

$$\longrightarrow \mathbf{C_{60}^{+}} + \mathbf{O_2^{+}} \quad (2c)$$

When C_{60}^{++} is passed through 2-10 mtorr of NH_3 at collision energies of 0.01 to 0.30 eV (E_{cm}) the ions detected are C_{60}^{+} *(720 amu)*, $C_{60}NH_2^{+}$ *(736 amu)*, $C_{60}NH_2NH_3^{+}$ *(753 amu)*, $C_{60}NH_2(NH_3)_2^{+}$ *(770 amu)* and $C_{60}NH_2(NH_3)_3^{+}$ *(787 amu)* which are shown in Figure 1. Other ions also observed include NH_4^{+}, $NH_4NH_3^{+}$ and the unreacted C_{60}^{++}. The mass assignment of these product ions were confirmed through the use of ND_3 as a target gas. We note that the $C_{60}NH_3^{++}$ ion is not observed under any conditions. A possible mechanism for the reaction with ammonia is as follows (the ions which we directly observe are shown in bold face):

$$\mathbf{C_{60}^{++}} + NH_3 \longrightarrow \{C_{60}^{+} - NH_3^{+}\} \quad (3)$$

$$\{C_{60}^{+} - NH_3^{+}\} + NH_3 \longrightarrow \mathbf{C_{60}^{+}} + \mathbf{NH_4^{+}} + NH_2 \quad (4a)$$

$$\longrightarrow \mathbf{C_{60}NH_2^{+}} + \mathbf{NH_4^{+}} \quad (4b)$$

$$\mathbf{C_{60}NH_2^{+}} + n\,NH_3 \longrightarrow \mathbf{C_{60}NH_2^{+}(NH_3)_{1\text{-}3}} \quad (5)$$

$$\mathbf{NH_4^{+}} + NH_3 \longrightarrow \mathbf{NH_3NH_4^{+}} \quad (6)$$

The relative abundance of all product ions are highly dependent on the ammonia gas pressure and collision energy, as shown in Figure 2. The inverse dependence of product ion abundance on collision energy may indicate that an exothermic reaction is taking place.[13,14] We feel that the NH_2 addition to the cationic fullerene (reaction 4b) indicates the production of either a fullerene amine or a protonated fullerene aziridine. Based on the previous characterization of the $C_{60}O$ species as an epoxide[9], we feel that the $C_{60}NH_2^{+}$ species corresponds to the formation of a protonated aziridine whose structure is shown as an insert in Figure 1.

For both the amine and aziridine structures, the two projecting hydrogens from $C_{60}NH_2^+$ should be highly susceptible to hydrogen bonding, therefore favoring a doubly coordinated species. Indeed we do observe the preference for the formation of $C_{60}NH_2(NH_3)_2^+$ at high ammonia pressures. Further support for this effect comes from the collision energy regime required for removal of the two bound NH_3's molecules. The collision energy dependence for the production of $C_{60}NH_2^+$ appears to be quite distinct from the $C_{60}NH_2^+(NH_3)_{1\text{-}3}$ ions (Figure 2b) suggesting that the NH_3's are indeed more weakly associated than the NH_2.

The reactivity of ammonia and oxygen with C_{60}^{++} correlates with the low ionization energies (IE's) of these molecules[15], as shown in Table I. The IE's for C_{60} and C_{60}^+ are 7.6 eV[16] and 12.25 eV[17] respectively. One would expect that a charge transfer reaction will only occur if the IE of the target molecule is below 12.25 eV, as illustrated in reaction (7).

$$C_{60}^{++} + M \longrightarrow \{ C_{60}^{+} - M^{+} \} \quad IE(M) < 12.25\ eV \quad (7)$$

While this energy release is sufficient to ionize either ammonia or oxygen, other gases having an IE larger then 12.25 eV (Table I) should not react with C_{60}^{++}. Indeed, we have found that the passage of C_{60}^{++} through such gases (He, Ar, N_2, & CH_4) at low collision energy exhibits no reactivity.

In conclusion, we have observed an associative charge exchange reactions for C_{60}^{++} with oxygen and ammonia which does not occur for C_{60}^{+} under identical experimental conditions. We believe that this is indicative of a new family of charge exchange reactions for C_{60}^{++} which will occur for any molecule whose IE lies below the IE of C_{60}^{+} (12.25 eV)[17]. This line of reasoning suggests that the inertness of C_{60}^{+} is due to the relatively low IE of C_{60}, which prevents direct charge transfer reactions from occurring. Our work also suggests that C_{60}^{+} may undergo similar charge exchange reactions with molecules whose IE lies below 7.6 eV. We are now in the process of examining this as well as gas phase chemistry for other C_n^{m+} ions.

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Table 1

Ionization Energies for Molecules Used in this Study

Molecule	**IE (eV)**
O_2	10.2 [15]
NH_3	12.0 [15]
C_{60}^+	*12.25* [17]
CH_4	12.6 [15]
N_2	15.6 [15]
Ar	15.7 [18]
He	24.6 [18]

Figure Captions

FIGURE 1 :
Product ions produced from the reaction of C_{60}^{++} + NH_3. The pressure of ammonia in the collision cell is 7.4 mtorr; the collision energy is 0.10 eV_{cm}. Note that the multiple peaks for each species result from the natural abundances of ^{13}C. The inset figure shows a proposed structure for the $C_{60}NH_2^+$ ion.

FIGURE 2:
The key to the symbols used in this figure is as follows:

● C_{60}^{++} Δ $C_{60}NH_2^+$ ❑ $C_{60}NH_2(NH_3)_2^+$

a) Percent total ion intensity of product ions produced from C_{60}^{++} + NH_3 reactions as a function of ammonia pressure in the target cell. The collision energy is 0.10 eV_{cm}.

b) Percent total ion intensity of product ions produced from C_{60}^{++} + NH_3 reactions as a of collision energy. The pressure of ammonia in the collision cell is 7.3 mtorr.

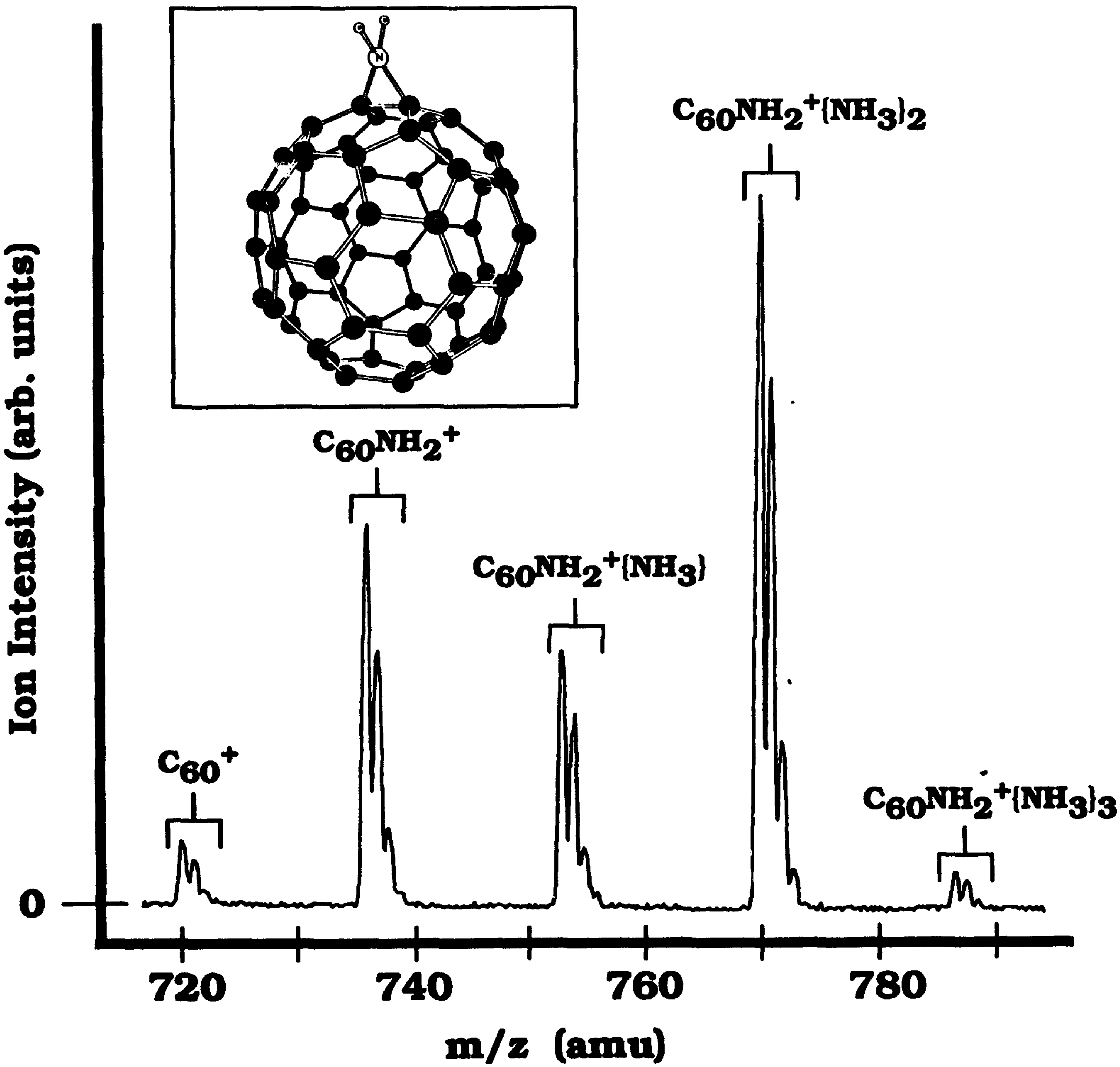
C_{60}^{+}
$C_{60}NH_2^{+}$
$C_{60}NH_2^{+}\{NH_3\}$
$C_{60}NH_2^{+}\{NH_3\}_2$
$C_{60}NH_2^{+}\{NH_3\}_3$
Ion Intensity (arb. units)
0
720
740
760
780
m/z (amu)

Figure 1

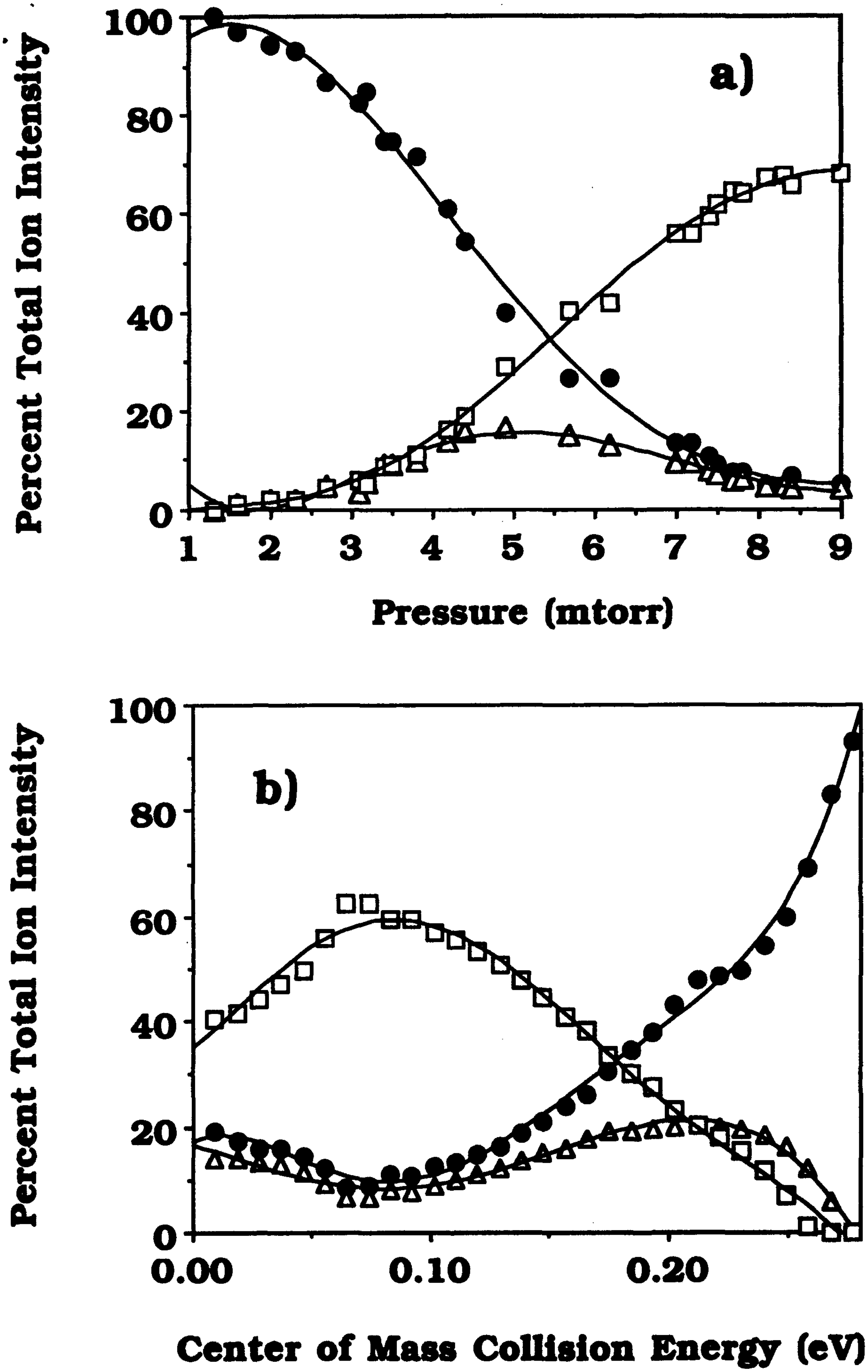
a)
Percent Total Ion Intensity
Pressure (mtorr)
b)
Percent Total Ion Intensity
Center of Mass Collision Energy (eV)

Figure 2