Formation of Long-Lived Highly-Excited States of H, C, and N Atoms by Low-Energy Electron Impact on CH_3CN

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Long-lived excited states of hydrogen, carbon and nitrogen atoms (H**, C** and N**) produced by the electron bombardment of CH_3CN in the energy range from 20 to 100 eV were detected as H^+, C^+ and N^+ ions as a result of collisions with H_2O. The appearance potential of H^+ was observed to be about 3 eV lower than the threshold energy for He^+ formed from He** with H_2O (about 24.6 eV). The C^+ threshold energy was about the same as that for He^+, while that for N^+ appeared to be a few eV higher. This suggests that the H** species is mainly responsible for the formation of CH_3CN^- due to the electron bombardment of CH_3CN observed by Sugiura and Arakawa, at least in the energy region below the He** threshold energy.

Since the formation of long-lived highly-excited Rydberg states of atoms by electron impact was first observed by Čermák and Herman,[1] a number of investigations have been made on the formation mechanism and on the collision of such atoms with molecules.[2-6] The following three types of ionization processes of highly excited atoms (A**) in collisions with molecules (B or BC) are known:

$$A^{**} + B \longrightarrow A^+ + B + e \quad (1)$$

$$A^{**} + B \longrightarrow A^+ + B^- \quad (2)$$

$$A^{**} + BC \longrightarrow A^+ + B + C^- \quad (3)$$

The cross sections of these reactions have been estimated theoretically by Matsuzawa[7-9] and compared with experimental results.[4]

Recently, Sugiura and Arakawa[10] have observed the formation of a negative ion, CH_3CN^-, in a mixture of CH_3CN vapor and various rare gases by electron impact. They ascribed the formation of this ion to the reactions:

$$e + A \longrightarrow A^{**} + e \quad (4)$$

$$A^{**} + CH_3CN \longrightarrow A^+ + CH_3CN^-, \quad (5)$$

where A represents a He, Ne, Ar or Kr atom. This is an example of a reaction of type (2). Furthermore, they found that the CH_3CN^- ion was also produced from pure CH_3CN and that the CH_3CN^- intensity exhibited a second-order dependence with the gas pressure. Hence, they considered that the negative ion formation was due to the reactions:

$$e + CH_3CN \longrightarrow Y^{**} + Z + e \quad (6)$$

$$Y^{**} + CH_3CN \longrightarrow Y^+ + CH_3CN^-, \quad (7)$$

where Y** denotes an excited neutral fragment formed by the excitation of the electron to a high Rydberg state. The appearance threshold of CH_3CN^- was estimated to be 23.2±0.5 eV.

In the present study, the formation of the highly excited atoms, H**, C** and N**, from CH_3CN by the bombardment of electrons of 20—100 eV is reported. Among the three excited species, H** appeared at the lowest electron impact energy, while C** had nearly the same threshold energy as that of He**.

Experimental

The apparatus, which was described previously,[11,12] was evacuated to 2×10^{-6} Torr. The CH_3CN vapor was introduced into the excitation region (Fig. 1) through a multichannel orifice M and was subjected to electron impact. The total pressure of the vapor at the source S_1 was about 0.3 Torr. The filament was heated by a dc current of 6A operated at 5 V, and the electrons produced were accelerated by a voltage of from 20 to 100 V which was applied between the filament (measured at the low potential end) and electrode 3 in Fig. 1. The electron current measured at electrode 1 was 10—300 μA. The excited neutral species were separated from the accompanying ions by electrostatic potentials and were allowed to collide with the target H_2O molecules in the collision chamber C. The pressure of the H_2O target gas measured at the source S_2 was about 1 Torr. The ions produced in the collision chamber were measured by a quadrupole mass filter. The sample gas pressures were measured by oil manometers and Pirani gauges. In addition to H_2O, CH_3CN and CH_3OH were also used as target molecules.

The energy spread of the electrons was estimated to be a few eV. The energy scale was calibrated by measuring the He^+ ions formed under similar conditions from He**, *i.e.*, produced by the reactions:

$$e + He \longrightarrow He^{**} + e \quad (8)$$

$$He^{**} + H_2O \longrightarrow He^+ + H_2O + e \quad (9)$$

The appearance potential of He^+ formed from He** was assumed to be nearly equal to the inoization potential of He^+, 24.6 eV.[13]

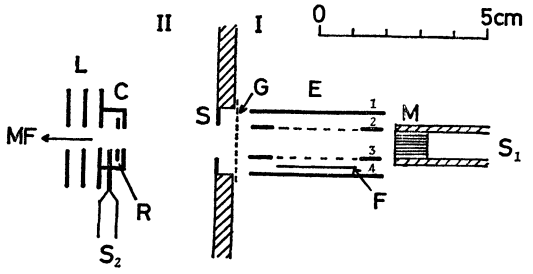

Fig. 1. Apparatus composed of Section I for producing long-lived highly-excited atoms by electron impact and section II, in which a collision chamber C and a mass filter MF are installed.
I: S_1, source of reactant molecules (CH_3CN); M, multichannel orifice; E, electron gun; F, tungsten filament; 1, electron trapping electrode; 2 and 3, exciting region; 4, repeller electrode; G, grid; S, slit. II: S_2, source of target molecule (H_2O); R, ion repeller electrode; L, ion lens system.

Results

The mass spectrum shown in Fig. 2 was obtained with H_2O as the target gas. Since the present study is concerned with the formation and ionization of H**, C** and N**, observed molecular ions, H_2O^+ *etc.*, were not analyzed in detail. The intensities of the H^+, C^+ and N^+ were found to be proportional to the electron current. In Fig. 3 the ion intensities divided by the electron currents are plotted as a function of the accelerating voltage. The intensities of H^+ and N^+ increased monotonically with increasing voltage, while the C^+ intensity curve had a shoulder at about 45 eV. The dependence of the H^+, C^+ and He^+ intensities on the electron accelerating voltage in the threshold region is shown in Fig. 4. The H^+ threshold appears to be about 3 eV lower than that for He^+, while the appearance potential of C^+ is nearly equal to the He^+ threshold.

The dependence of the ion intensities on the pressure of the target H_2O is shown in Fig. 5. The intensity I varies with the pressure p as

$$I \propto p \exp(-cp) \qquad (10)$$

This is demonstrated in Fig. 6, where $\log(I/p)$ values depend linearly on the gas pressure p. As discussed in Refs. 11 and 12, the behavior expressed by Eq. (10) can be accounted for as a result of the attenuation of the highly-excited atoms by collision with H_2O mole-

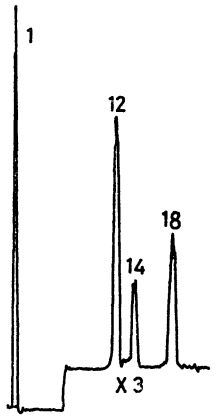

Fig. 2. Mass spectrum of the ions produced by collisions of highly-excited species from CH_3CN with H_2O. Electron accelerating voltage: 60 V, electron trap current: 200 μA, pressures of CH_3CN and H_2O: 0.13 and 0.4 Torr, respectively.

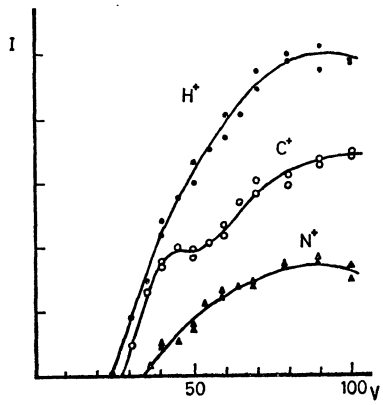

Fig. 3. Intensities of ions (in arbitrary units) divided by the electron trap current obtained for different electron accelerating voltages.

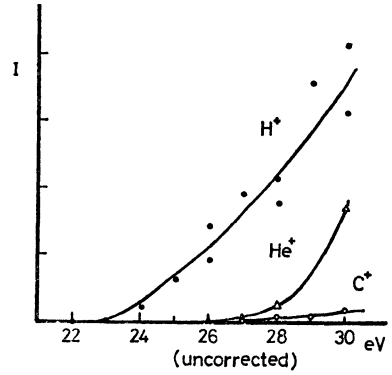

Fig. 4. Ion intensities (in arbitrary units) in the vicinity of threshold obtained for different electron bombardment energies.

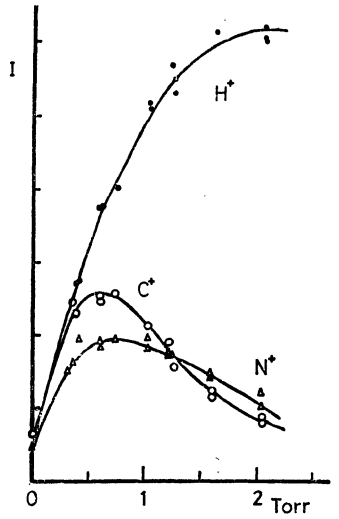

Fig. 5. Intensities of ions (in arbitrary units) plotted for different pressures of H_2O measured at S_2.

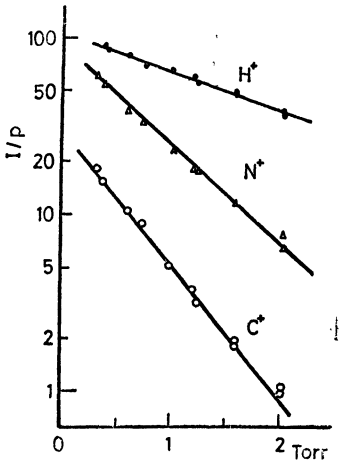

Fig. 6. Intensities of H^+, C^+ and N^+ displayed in Fig. 5 divided by the pressure p of H_2O measured at S_2 and plotted on a logarithmic scale as a function of p.

cules. The ion intensities do not tend to zero in the absence of target molecules, as shown in Fig. 5. This shows that the excited species can be ionized by collisions not only with the target gas but also with residual gases and/or the surface of the electrodes. The ion intensity varies with the pressure of the projectile molecule CH_3CN in a similar manner.

Ionization processes of the highly-excited atoms H**, C** and N** producing H^+, C^+ and N^+, respectively, were also observed when CH_3CN or CH_3OH was used as a target gas. The variations of the ion intensity, I, on the electron current and on the electron accelerating voltage were similar to those observed with H_2O as the target gas. The relation between I and the gas pressure p was also that given in Eq. (10).

Discussion

The uncorrected thresholds of H^+ and C^+ shown in Fig. 4 are shifted by about -1.4 eV with reference to that of He^+, as described in Experimental section, and compared with the appearance threshold of CH_3CN^- observed by Sugiura and Arakawa.[10] One can conclude that the essential part of the Y** species which they assumed in reactions (6) and (7) is H** at least in the range below the threshold of He**, since this species seems to be the only reactive species formed in this electron energy range. The C** and N** species can also contribute to molecular negative-ion formation at higher electron energies.

The threshold energy for H^+, which was thus estimated to be about 21.5 eV with a range of uncertainty of about 1.5 eV, seems to differ slightly from that for CH_3CN^- reported by Sugiura and Arakawa, 23.2 ± 0.5 eV; however, a more precise description of the threshold behavior requires a further critical experiment.

The shoulder appearing in the efficiency curve of C** suggests that the curve is composed of two separate efficiency curves which correspond to the C** species arising from the methyl and the nitrile carbon atoms in CH_3CN.

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