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Emission Spectra of Carbon Disulfide, Hydrogen Sulfide, and Thiols by Controlled Electron Impact

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The emission spectra in the 200—600 nm region produced by the controlled electron impact method were investigated in the vapor phase on hydrogen sulfide, carbon disulfide, methanethiol, and ethanethiol at low pressures. The photoemissions were observed and assigned for an excited parent molecule, molecular ions, and fragments, such as CS_2, CS_2^+, H_2S^+, H, CH, CS, and HS^+. The intensities of the photoemission of most of the species were found to increase linearly with both the electron beam current and the gas pressure, and these species were concluded to be produced in some one-electron unimolecular processes.

The formation of excited molecules and excited molecular ions and their emission spectra have been investigated by a number of methods for excitation, such as by photons, flames, or electric discharges.[1] Although these methods are useful for chemical analyses, secondary reactions induce difficulties in a detailed analysis of the mechanism of fragmentation and excitation processes of the species concerned. A crossed-beam technique, in which the molecular vapor is excited by a controlled electron source, has been employed in recent years to overcome the above difficulties.[2] Since the gas pressure can be kept very low in the controlled electron impact method, the effect of molecular collisions is greatly reduced and, consequently, the bands of the primarily excited species appear with relatively high intensity. It is, therefore, possible to observe primary reactions more accurately; this may lead not only to the elucidation of the fragmentation processes of the parent molecule, but also to the information about the collision phenomena.

The emission spectra of aromatic molecules by controlled electron impact have been reported by the present authors.[3] Those of CS_2 and H_2S have been measured by Smith[4] and by Horani *et al.*[5,6] respectively, and the bands of CS ($A^1\Pi—X^1\Sigma^+$), CS_2^+ ($\tilde{B}^2\Sigma_u^+—\tilde{X}^2\Pi_g$), HS^+ ($A^3\Pi—X^3\Sigma^-$), and H_2S^+ ($A^2A_1—\tilde{X}^2B_1$) have been observed and assigned. In the present paper, the emission spectra of carbon disulfide, hydrogen sulfide, methanethiol, and ethanethiol under excitation by a controlled electron beam will be presented, and the mechanism of the excitation will be discussed in relation to the intensity measurements.

Experimental

The experimental method used in the present work has been described in detail in the previous papers.[3,7] The electrons from a heated tungsten filament were accelerated and introduced into the collision chamber through a slit (2 × 15 mm). The energies of the electrons were externally controlled from 15 to 300 eV. The sample gas was jetted through a nozzle (0.1 mm in diameter) and collided with the electron beam. The pressure during the operation, as measured with a Penning gauge, was of the order of 10^{-4} mmHg, though the density of the gas in the middle of the molecular jet was higher. The photoemission produced by collisions between electrons and molecules was measured photoelectrically with either a Jarrell Ash JE-25 or a JASCO CT-50 monochromator.

The H_2S was obtained from the Takachiho Chemical Ind., while the D_2S was prepared from FeS and D_2SO_4. The HDS[8] was prepared from FeS and a 1:1 mixture of H_2SO_4 and D_2O. The methanethiol was purchased from the Matheson Co., and the CS_2 and the ethanethiol, from the Wako Pure Chemical Ind. The samples were frozen and degassed repeatedly before use.

Results and Discussion

Carbon Disulfide. A typical emission spectrum of carbon disulfide in the 220—320 nm region is shown in Fig. 1. The impact energy was 100 eV with the electron beam current of 100 μA. The spectrum is in good agreement with the published one; the bands around 260 nm are assigned to CS ($A^1\Pi—X^1\Sigma^+$) and the most intense bands at 282 and 285 nm to CS_2^+ ($\tilde{B}^2\Sigma_u^+—\tilde{X}^2\Pi_g$).[4]

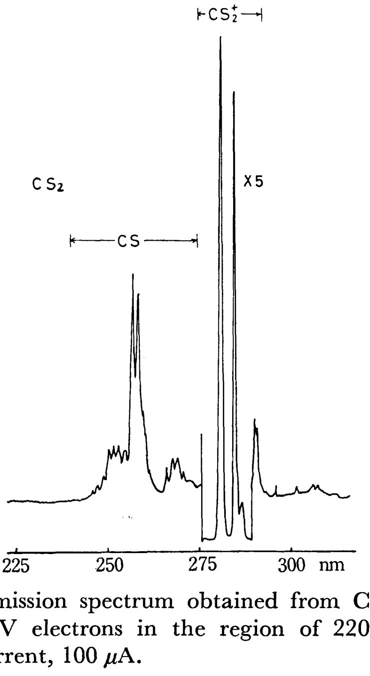

Fig. 1. Emission spectrum obtained from CS_2 excited by 100 eV electrons in the region of 220—320 nm. Beam current, 100 μA.

A typical spectrum of carbon disulfide in the 300—650 nm region is shown in Fig. 2. There seem to be two emission systems in this region, judging from the different intensity ratios for various impact energies. The first one is a continuous band extending from 340 to 640 nm. The second one, which is superimposed

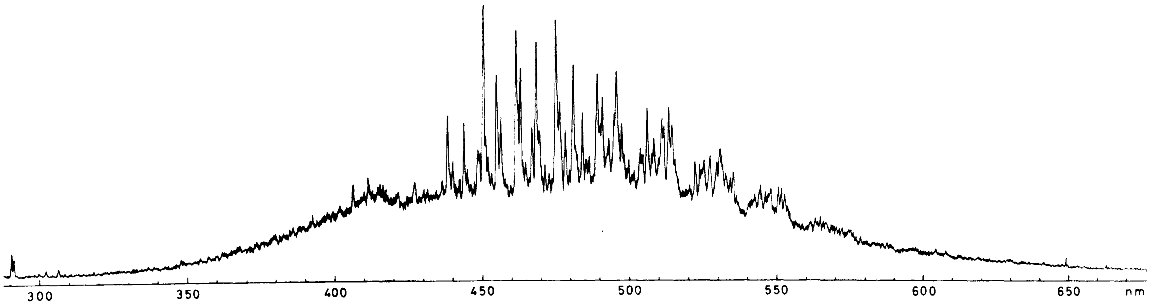

Fig. 2. Emission spectrum obtained from CS_2 excited by 200 eV electrons in the region of 300—650 nm. Beam current, 250 μA.

on the first one, is much sharper, shows a vibrational structure, and disappears much more rapidly than the other at lower impact energies. The intensities of the photoemission of these bands were determined for various currents of the incident electrons and were found to be proportional to the electron beam current, as is shown in Fig. 3.

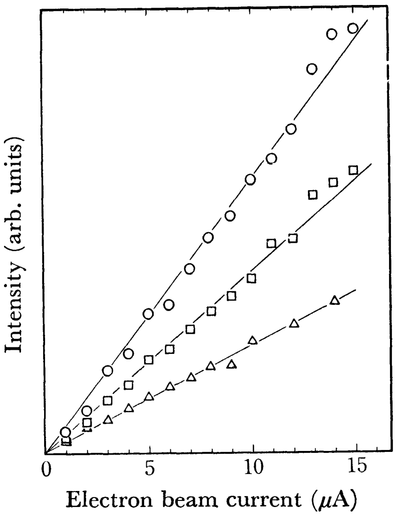

Fig. 3. Dependence of photoemission intensities of CS_2 (△), CS_2^+ (A–X transition) (○) and CS_2^+ (B–X transition measured in the second order) (□) from CS_2 on electron beam current. Electron energy was 200 eV.

The first band system in the 300—650 nm region is similar to the one observed in the discharge[9] and has been assigned to the CS_2 fluorescence. Arnold and Kimbel proposed a three-body recombination mechanism for this emission. In the present study, however, the pressure in the collision chamber is so low ($<10^{-2}$ mmHg) that the intermolecular collision seems to be negligible. An alternative suggestion as to the mechanism for the emission of CS_2^* in the present research would be a direct excitation of CS_2;

$$CS_2 \xrightarrow{e} CS_2^* \longrightarrow CS_2 + h\nu$$

The linearity of the emission intensity to the electron beam current supports this mechanism. Furthermore, the finding that the intensity of this band relative to that of CS_2^+ at 282 nm did not vary with the pressure supports the above conclusion.

The second band system has complicated vibrational structures; the apparent intensity of the 449 nm band (the strongest one in this region) is about 1/10 of that of the 282 nm band of CS_2^+ (the quantum efficiency was not calibrated). The emission intensities of these bands are also proportional to the electron beam current and to the gas pressure, as are shown in Figs. 3 and 4 respectively. These facts suggest that the emitting species are produced directly from the parent molecules, as are those of the first band. The emission spectra of a mixture of CS_2 and H_2 was measured by this method as well as that of CS_2 and H_2S. The spectra were superpositions of the bands of the two parent molecules. These bands also appeared in the spectrum of methanethiol; in this case the intensity ratio between the band at 449 nm and that at 282 nm (CS_2^+) is about 1/10 as it is in the case of carbon disulfide, though the intensity of CS_2^+ from methanethiol is much smaller than that of CS. Among the possible photoemitting species of these bands, such as CS_2, CS, C, S or their ions, the complicated appearance of the band and related data in the literature[1,10] make it possbile to exclude the atomic species. If they were CS or CS^+, they should appear in the cases of thiols and methyl phenyl sulfide with much higher intensities. Furthermore, the A–X transition of the CS radical is in the region of 240—290 nm,[1] which is not coincident with that of the second bands. The adiabatic and the vertical transition energies of CS_2^+ to the first excited

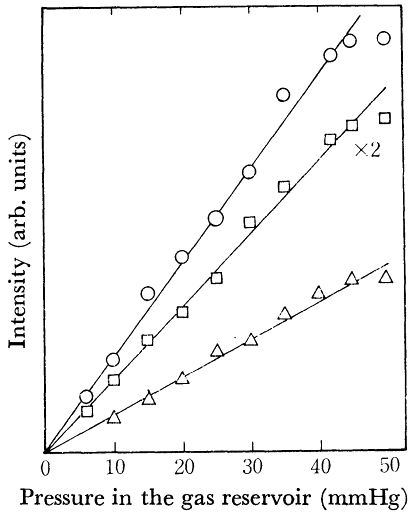

Fig. 4. Dependence of photoemission intensities of CS (△), CS_2^+ (A–X transition) (○) and CS_2^+ (B–X transition) (□) on gas pressure in the gas reservoir. Electron energy was 300 eV and beam current, 20 μA.

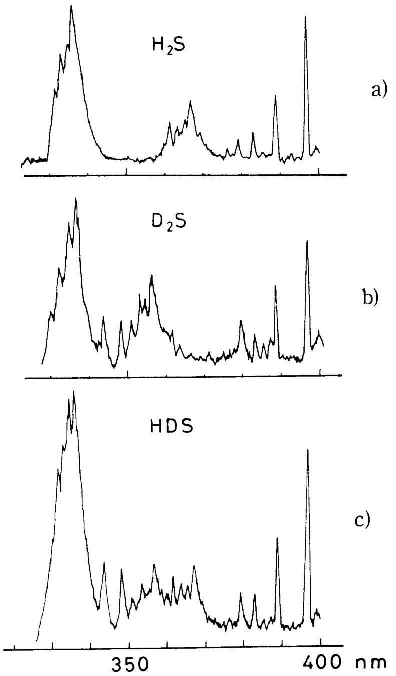

Fig. 5. Emission spectra obtained from H_2S (a), D_2S (b) and HDS[8] (c) excited by 200 eV electrons. Beam current, 500 μA.

state were determined to be 2.63 eV (472 nm) and 2.77 eV (448 nm).[11] The latter coincides with the position of the strongest band in the present spectrum. These results suggest that this second band can be assigned to CS_2^+ ($A^2\Pi_u$—$\tilde{X}^2\Pi_g$).

Hydrogen Sulfide. Some typical emission spectra of H_2S, D_2S, and HDS[8] in the region of 330—400 nm are shown in Fig. 5. The impact voltage was 200 V and the electron beam current was 500 μA in these measurements. The sharp lines at 486, 434, 410, 397, and 389 nm, which have been observed for all the molecules containing the hydrogen atom, are assigned to the hydrogen Balmer series. There are two intense bands at about 336 nm and at about 366 nm in the spectrum of H_2S; the latter seems to shift toward the shorter wavelength side, at about 357 nm, in the spectrum of D_2S. The spectrum of HDS may be regarded as a superposition of those of H_2S and D_2S. This finding suggests that these bands are related to a diatomic molecule containing both a hydrogen and a sulfur atom. This is confirmed by the facts that these bands also appeared in the spectra of methanethiol, ethanethiol, and benzenethiol, whereas they did not appear in CS_2, H_2, methyl phenyl sulfide or thiophene, which have no H–S bond; they may not form such species as HS since two-body collisions are infrequent at the pressure of $10^{-2\sim-3}$ mmHg. The A–X transition of the HS radical was observed below 324 nm[1] and seems to be undetectable in the emission because of predissociation.[12] Thus these bands can be assigned to the A–X transition of HS^+ and DS^+ radicals, as Horani *et al.* indicated.[5] The separations between successive bands of HS^+ and DS^+ are estimated to be 2470±100 cm^{-1} and 1790±100 cm^{-1} respectively. The former value is slightly smaller than that between

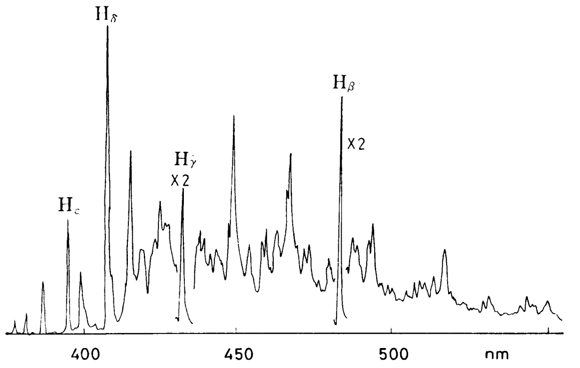

Fig. 6. Emission spectrum obtained from H_2S excited by 200 eV electrons in the region of 400—550 nm. Beam current, 500 μA.

successive bands of the HS radical in the ground state, 2582 cm^{-1}.[13] The difference in the separation between HS^+ and DS^+ may be interpreted as an isotopic shift; this finding also confirms the above assignment.

There are a number of prominent bands in the 400—550 nm region, as is shown in Fig. 6. These bands, except for the hydrogen Balmer series, were not observed in other molecules, such as methanethiol, ethanethiol, hydrocarbons, carbon disulfide, and thiophene. The observed spectrum of a mixture of CS_2 and H_2S was simply a superposition of the spectra of the parent molecules. This finding also suggests that the excited species come directly from the parent molecule, and the band can be assigned to H_2S^+, as did the previous authors.[6]

A number of MO calculations[14] on this molecule have been reported. If Koopmans' theorem holds in this molecule, the energy difference between the ground and the first excited states of H_2S^+ is estimated to be about 2.7 eV (459 nm). The adiabatic and the vertical transition energies between $^2A_1$—$^2B_1$ were determined to be 2.28 eV (544 nm) and 2.77 eV (448 nm) respectively in photoelectron spectroscopy.[11] The latter value

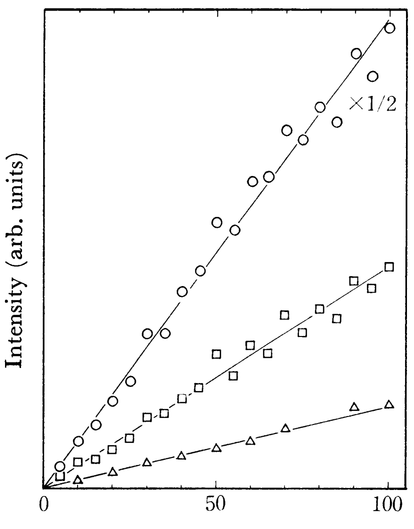

Fig. 7. Dependence of photoemission intensities of HS^+ (○), H (□) and H_2S^+ (△) on electron beam current. Electron energy was 200 eV.

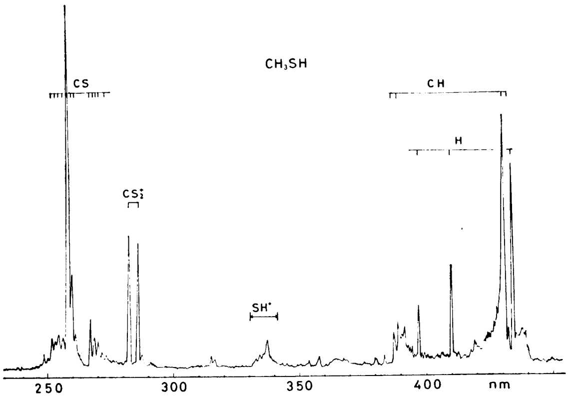

Fig. 8. Emission spectrum obtained from methanethiol excited by 200 eV electrons. Beam current, 400 μA.

is in good agreement with the strongest band of the H_2S^+ in the present work.

The intensities of the photoemission of H, HS^+, and H_2S^+ from H_2S for various electron beam currents are shown in Fig. 7. The linearity also holds for ethanethiol and proves that these species are excited in single-electron processes.

Thiols. A typical emission spectrum of methanethiol was observed by electron impact at 200 eV and a beam current of 1 mA, as is shown in Fig. 8. The spectrum of ethanethiol was similar to that of methanethiol except for the relative intensites of the fragments. The Balmer series of hydrogen is also the most prominent. The emission bands at 431 and 387 nm were assigned to the (0,0) bands of the CH radical in the $A^2\Delta$—$X^2\Pi$ and $B^2\Sigma^-$—$X^2\Pi$ transitions respectively. The bands at 282 and 285 nm were assigned to the CS_2^+ ion and the bands around 260 nm to the CS radical, as in the case of CS_2. In this case, however, the bands of CS are much more intense than those of CS_2^+ which would not be formed by a simple collision between an electron and a CH_3SH molecule.

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