UV and Visible Fluorescences of CF_3 Radicals Produced by the Two-photon Decomposition of CF_3Br and Their Radiative Lifetimes

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Synopsis. The UV and visible emission bands of the CF_3 radical were observed in the two-photon decomposition of CF_3Br using KrF excimer laser (248 nm) radiation. Very short radiative lifetimes (shorter than 40 and 50 ns for the UV and visible bands, respectively) were obtained.

Knowledge of the excited states of the CF_3 radical is important in both semiconductor-device fabrication[1] and regarding ozone depletion in the stratosphere.[2] Two emission bands of CF_3 radicals were observed in the UV (170—320 nm) and visible (400—750 nm) regions by the VUV (100—140 nm) photolysis of CF_3X molecules (X=H, Cl, Br) recently.[3] In the present study, the observation of the UV and visible emissions of CF_3, produced by the two-photon decomposition of CF_3Br, were investigated using KrF excimer laser light (248 nm). Also, measurements of the radiative lifetimes of both emission bands were attempted. Since both UV and visible emission bands of CF_3 were observed in the photolysis of CF_3Br by the Kr resonance line (123.6 nm) in the previous study, these emission bands can be produced by the two-photon photodecomposition of CF_3Br by the KrF excimer laser (248 nm).

$$CF_3Br + 2h\nu(248\text{ nm}) \longrightarrow CF_3^* + Br \qquad (1)$$

Further, if the radiative lifetimes of both bands are longer than the experimental response, these values can be obtained directly using a laser pulse.

The KrF excimer laser (Lamda Physik EMG 102) beam was focussed in a stainless steel fluorescence cell through a quartz lens. The emission was collected at a right angle to the laser beam (using an optical system consisting of three quartz lenses) and was dispersed with a 0.35-m monochromator (McPherson Model 270). Since fluorescence was measured in the UV and visible regions, two gratings (1200 grooves/mm) blazed at 250 and 500 nm were used. A glass filter (Schott Glaswerke, GG 475, transmission longer than 470 nm) was used in the measurement of the visible emission spectrum. Fluorescence signals were detected with a photomultiplier (EMI 9635 and 9558B for UV and visible, respectively) and processed by a boxcar integrator (PAR 162).

When laser light was focussed through a quartz lens in the CF_3Br gas, a very bright-yellow emission was visible from the cell. The measured UV emission band is shown in Fig. 1a. The pressure of CF_3Br in the cell was kept at 133 Pa and the gas was slowly pumped using a rotary pump. The discrete emission band observed in the region of 200—225 nm corresponds to the UV emission band of CF_3.[3] The spectral profile is quite similar to that observed previously and separations of the characteristic progression (shown by arrows, 1000—1050 cm^{-1}), correspond to the ν_1 mode of CF_3.[3] The emission appearing at 193 nm should originate from the resonance fluorescence of the excited carbon atoms,[4] $C(3^1P^0 \xrightarrow{193\text{ nm}} 2^1D)$, after the resonance absorption from $C(^1S)$, $C(3^1P^0 \xleftarrow{248\text{ nm}} 2^1S)$. The excited carbon atom, $C(^1S)$, might be produced during the multi-photon decomposition of CF_3Br. The strong emission band (starting at 220 nm) corresponds to the $CF(A^2\Sigma \rightarrow X^2\Pi)$ system.[5] Essentially, the UV emission band of CF_3 should extend to 300 nm, having a maximum at 240 nm. In the present experimental system, however, the emission band of the $CF(A \rightarrow X)$ system was too strong and the UV band of CF_3 can be identified only in the region from 200 to 220 nm. The strong emission band of the $CF_2(^1B_1 \rightarrow {}^1A_1)$ system was observed in the region from 250 to 350 nm and an unidentified strong emission band was present up to 450 nm.

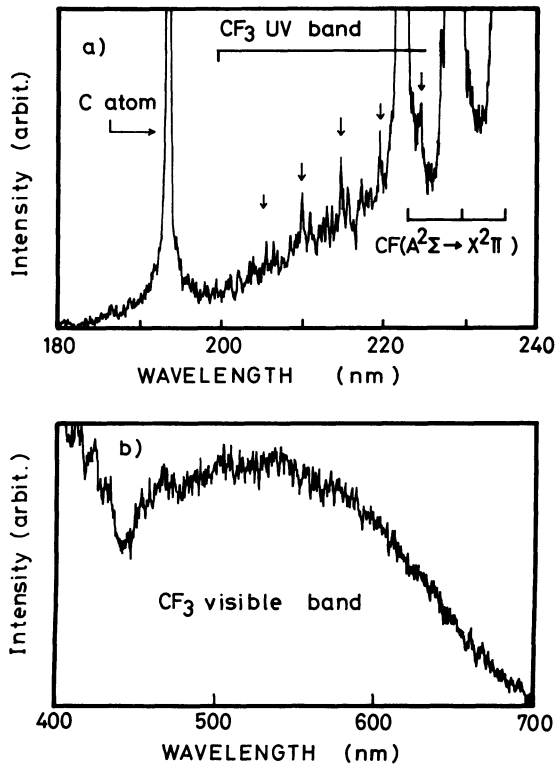

Fig. 1. Emission spectra of the UV (a) and visible (b) bands of CF_3 produced in the two-photon decomposition of CF_3Br by the KrF excimer laser (248 nm) radiation.

The observed visible emission-band spectrum is

shown in Fig. 1b. The continuous emission band (devoid of structure) in the region from 450 to 700 nm is also the same as that observed previously.[3] Since both UV and visible bands were observed, a two-photon decomposition of CF_3Br occured by Reaction (1), although other excited species (such as C, CF, and CF_2) were produced in this system.

The measurements of the radiative lifetimes were carried out at 210 nm for UV and 600 nm for the visible band (under 1 nm of spectral resolution). Fluorescence signals detected by photomultipliers were digitized by a transient digitizer (Tektronix R7912, 1 ns of time resolution) and processed by a minicomputer (DEC, LSI 11). Since the pulse of the KrF laser was 16 ns (fwhm) and the time response of the photomultipliers was about 25 ns (fwhm), radiative lifetimes could be obtained if the lifetime was longer than 50 ns (reliable value should be longer than 100 ns). The apparent radiative lifetimes measured at 27—667 Pa of CF_3Br were 30—40 ns for the UV band and 40—50 ns for the visible band. These lifetime values are shorter than the reliable instrumental time response. Therefore, it is concluded that radiative lifetimes for the UV and visible bands are shorter than 40 and 50 ns, respectively. No significant pressure dependence of the lifetime was observed for both measurements.

Very short radiative lifetimes were obtained for UV and visible band emissions of CF_3. Results are reasonable for the allowed transition of a polyatomic molecule. Using theoretical calculations[3] regarding the CF_3 electronic states, the UV band has been tentatively assigned to a Rydberg state (D_{3h} structure) emitting to the ground state ($2A'_1 \rightarrow 1A''_2$), while the visible band is thought, based on emission quenching experiments, to arise from transitions from the 1E′ and/or $2A_2''$ Rydberg states (D_{3h}) to a repulsive state ($1A_1'$). The fluorescence quantum yields of the UV and visible band from the photolysis of CF_3Br at 124 nm were determined to be 1 and 5%, respectively.[3] It is possible that the predissociation occurs in both the upper states by the coupling of the potential curves of the lower electronic states. Short radiative lifetimes were obtained.

Recently, lifetime measurements regarding the UV and visible emission bands of CF_3 were carried out by two groups using synchrotron-radiation tequniques[6] and pulsed VUV laser (121 nm) radiation.[7] The former obtained fluorescence lifetimes of 14—17 ns for both the UV and visible bands and the later gave those of 15±3 and 18±3 ns for the UV- and the visible-band emissions, respectively.

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