

# FLUORESCENCE PROPERTY AND ITS MAGNETIC FIELD DEPENDENCE ACROSS THE PHOTODISSOCIATION THRESHOLD OF CH<sub>3</sub>CHO AND CD<sub>3</sub>CDO IN A SUPERSONIC JET\*

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*(Received 13 March 1993)*

Fluorescence characteristics of jet-cooled acetaldehyde at zero field is confirmed to change from the small molecule behavior to the statistical limit behavior in CH<sub>3</sub>CHO and to the intermediate case in CD<sub>3</sub>CDO, as the excitation energy increases across the dissociation threshold located below 320 nm. The excitation energy dependence both of the intensity and of the lifetime of the slow fluorescence shows that the dissociation rate becomes faster abruptly with increasing excess energy above the threshold, and the excess energy dependence above the threshold seems to be more drastic in CH<sub>3</sub>CHO than in CD<sub>3</sub>CDO. External magnetic field as well as the dissociation in the triplet state plays a role to increase the level density of the triplet state coupled to S<sub>1</sub>. On excitation below the dissociation threshold, the magnetic quenching of fluorescence becomes more efficient with increasing excess energy and the efficiency of the quenching is larger in CD<sub>3</sub>CDO than that in CH<sub>3</sub>CHO by a factor of about 2. On excitation above the threshold, however, the efficiency becomes lower with increasing excitation energy. Thus, the magnetic field effects on fluorescence also change drastically across the dissociation threshold.

**KEY WORDS:** Dissociation; fluorescence; magnetic field effect; acetaldehyde; supersonic jet; deuterium effect

## 1. INTRODUCTION

Magnetic field is one of the typical external perturbations which may be used to control chemical reactions. In solution, photochemical processes are well known to be affected by an external magnetic field ( $H$ ) when the radical pair formation participates in the processes.<sup>1</sup> The magnetic field effects in the photochemical and photophysical processes of gaseous molecules have been also examined through the fluorescence measurements.<sup>1,2</sup>

It was shown that fluorescence intensity and decay profile are strongly affected by  $H$  in some azaaromatic molecules.<sup>3–7</sup> The magnetic field effects observed in these azaaromatic molecules seem to be common to molecules having an effective singlet–

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\* Dedicated to Professor Mitsuo Ito on the occasion of his retirement from Tohoku University

triplet interaction; the number of the triplet states coupled to the singlet state is considered to increase with  $H$  as a result of field-induced mixing among different triplet spin sublevels. In order to confirm this hypothesis, however, we may have to carry out additional studies of the magnetic field effects on fluorescence of other kinds of molecule than the azaaromatic molecules in which singlet–triplet interaction is similarly strong.

Acetaldehyde seems to be one of the most suitable candidates for such a study since the  $S_1$  state of this molecule is considered to interact effectively with the triplet states.<sup>8,9</sup> In fact, fluorescence of acetaldehyde vapor is affected by  $H$ , as preliminary reported in a previous paper.<sup>10</sup> Further, fluorescence property of acetaldehyde vapor at zero field drastically changes at around 317 nm, suggesting that the photodissociation threshold is located at around this wavelength.<sup>11</sup> Both the experimental works<sup>11,12</sup> and the theoretical work<sup>13</sup> suggest that the dissociation occurs via higher vibrational levels of  $T_1$  reached by intersystem crossing. If the magnetic field induces a mixing among spin substates, as in the case of the azaaromatic molecules, and if the photochemical process depends on the spin state, the efficiency of the dissociation may be affected by  $H$  since the different spin states are populated from each other in the presence and in the absence of  $H$ .

Recently, photofragment excitation spectrum of HCO radical produced by dissociation of acetaldehyde vapor was obtained by Hanazaki and co-workers.<sup>14</sup> The dissociation threshold determined by the photofragmentation spectroscopy seems to be different from the one determined by the fluorescence spectroscopy. In order to examine the relation between the fluorescence properties and dissociation process, it seems to be necessary to examine the decay and intensity of fluorescence more carefully in a jet with excitation across the dissociation threshold.

In the present paper, we report in more detail the experimental results of the intensity and decay of fluorescence both at zero field and in the presence of  $H$  across the dissociation threshold of  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{CDO}$ .

## 2. EXPERIMENTAL

Commercially available  $\text{CH}_3\text{CHO}$  (Merck) and  $\text{CD}_3\text{CDO}$  (MSD Isotopes; 99% atomic percent) were used without further purification.

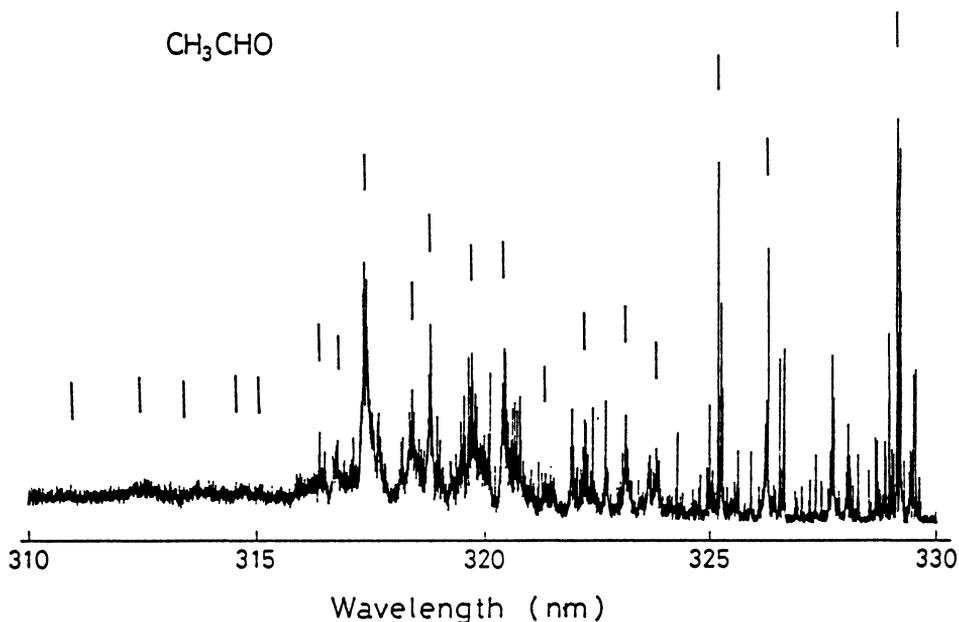
Fluorescence intensity and decay of both compounds were measured in a supersonic jet by monitoring undispersed fluorescence both in the absence and in the presence of  $H$ . The supersonic jet apparatus and the laser spectrometer used in the present study are the same as reported in previous papers.<sup>5–7,11</sup> Briefly, a gaseous mixture of acetaldehyde saturated at  $-15^\circ\text{C}$  and He with a total pressure of 1 atm is expanded into a vacuum chamber through a nozzle with a diameter of 0.4 mm to form a molecular beam. The second harmonics of the output of a dye laser (Lambda Physik FL2002) pumped by a XeCl excimer laser (Lambda Physik EMG 103MSC) was generated with a KDP crystal. The generated UV light with a duration of  $\sim 10$  ns and a spectral width of  $\sim 0.2$   $\text{cm}^{-1}$  irradiated the sample 22 mm downstream from the nozzle. In a traditional orthogonal geometry, the molecular beam proceeds along the

X axis, and the linearly polarized excitation light propagates along the Y axis with the polarization direction along the X axis. External magnetic field was applied along the Z axis. Fluorescence which propagates along the Z axis was monitored without polarizer for emission.

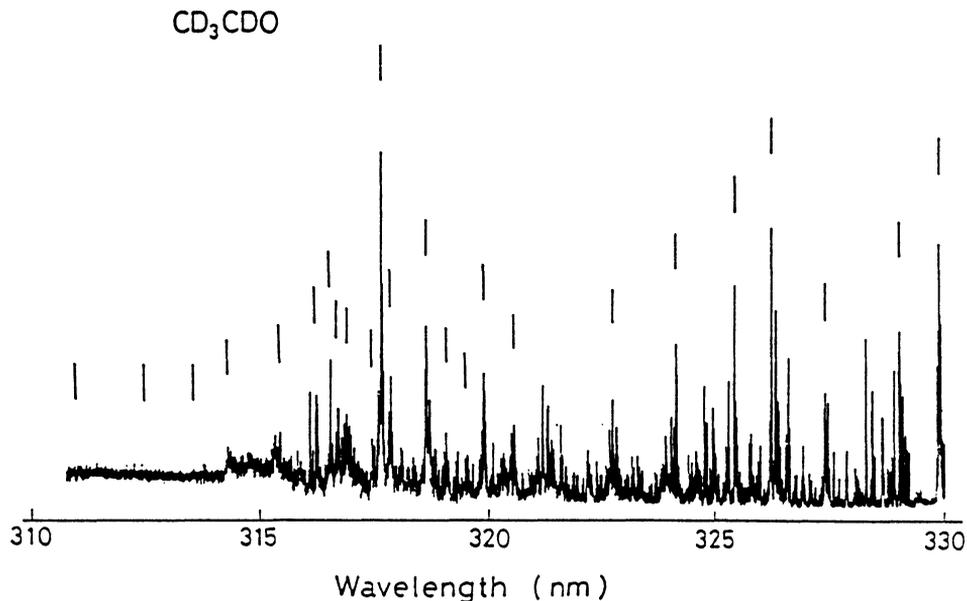
### 3. RESULTS AND DISCUSSION

#### 3.1. Fluorescence property at zero field

At first, fluorescence property of acetaldehyde vapor at zero field and its excitation energy dependence are discussed. Fluorescence excitation spectra in the region from 330 to ~310 nm measured in a jet at zero field are shown in Figures 1 and 2 for CH<sub>3</sub>CHO and CD<sub>3</sub>CDO, respectively. The fluorescence excitation spectra in the low frequency region of the S<sub>0</sub> → S<sub>1</sub> transition of both compounds in a jet were reported by Lee and co-workers.<sup>15,16</sup> They assigned the origin of the S<sub>0</sub> → S<sub>1</sub> transition at 29,771 and 29,808 cm<sup>-1</sup> in CH<sub>3</sub>CHO and CD<sub>3</sub>CDO, respectively. Their vibronic assignment showed the active modes to be the methyl internal rotation  $\nu_{15}$ , the C=O out-of-plane wagging  $\nu_{14}$ , and the CCO in-plane bending  $\nu_{10}$  in both compounds, though their vibronic assignment was limited to the bands located below 1000 cm<sup>-1</sup> above the S<sub>0</sub> → S<sub>1</sub> origin. The excitation spectrum of CH<sub>3</sub>CHO in a jet was reported



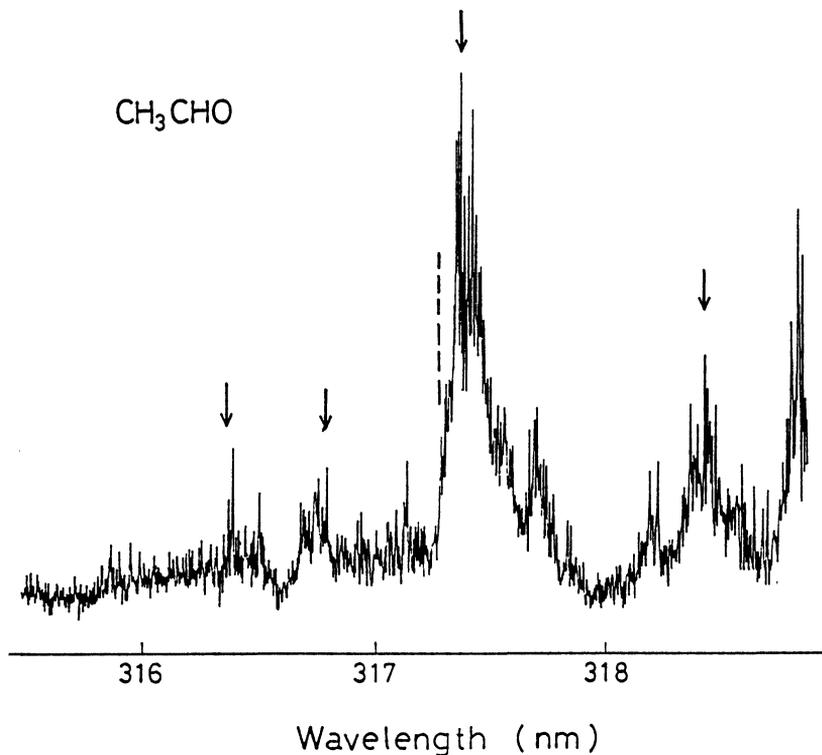
**Figure 1** Fluorescence excitation spectrum of CH<sub>3</sub>CHO in a jet from 330 to 310 nm. Vertical lines indicate the excitation position where the magnetic field dependence of fluorescence intensity was examined.



**Figure 2** Fluorescence excitation spectrum of  $\text{CD}_3\text{CDO}$  in a jet from 330 to ~310 nm. Vertical lines indicate the excitation position where the magnetic field dependence of fluorescence intensity was examined.

also by Baba et al.,<sup>17</sup> and the vibrational analysis was done for the vibronic bands located at wavelengths longer than 317.4 nm. As pointed out by Baba et al. for  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{CDO}$ , it is noticed in Figures 1 and 2 that fluorescence intensity markedly decreases with decreasing excitation wavelength beyond 317 nm both in  $\text{CH}_3\text{CHO}$  and in  $\text{CD}_3\text{CDO}$  and that peaks could not be resolved at shorter wavelengths below 315 nm in  $\text{CH}_3\text{CHO}$  and below 314 nm in  $\text{CD}_3\text{CDO}$ . The expanded view of the fluorescence excitation spectra at around 317 nm are shown in Figures 3 and 4 for  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{CDO}$ , respectively.

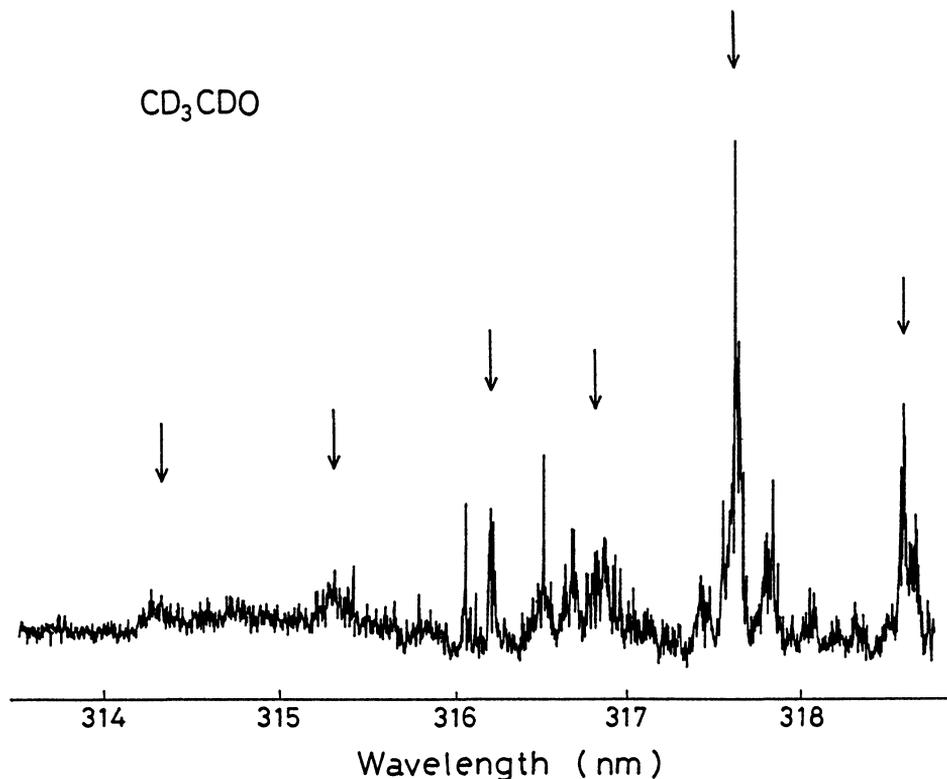
It is considered that dissociation occurs following photoexcitation into higher vibrational levels of  $S_1$  of acetaldehyde vapor with a threshold below 320 nm:  $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3 + \text{CHO}$ .<sup>18,19</sup> As shown in the previous paper,<sup>11</sup> both the quantum yield and the decay of fluorescence at low pressures in a bulk gas drastically change as the excitation wavelength becomes shorter across the photodissociation threshold; as the excitation energy increases across the threshold, the fluorescence characteristics changes from the small molecule behavior to the statistical limit through the intermediate case behavior. The sudden decrease in fluorescence quantum yield is confirmed also in the jet under collision-free conditions, as mentioned above (see Figures 1 and 2). Interestingly, the fluorescence intensity of  $\text{CH}_3\text{CHO}$  seems to drop more rapidly with decreasing excitation wavelength, in comparison with  $\text{CD}_3\text{CDO}$  (cf. Figures 3 and 4), implying that the dissociation efficiency changes more rapidly in  $\text{CH}_3\text{CHO}$  than in  $\text{CD}_3\text{CDO}$  as the excitation energy increases. The dissociation threshold in  $\text{CH}_3\text{CHO}$  may be estimated to be at 317.25 nm from the sudden drop



**Figure 3** An expanded view of the fluorescence excitation spectrum of CH<sub>3</sub>CHO at around 317 nm. A broken line indicates the dissociation threshold estimated from the excitation spectrum. Arrows indicate the excitation positions where fluorescence decays shown in Figure 5 were observed.

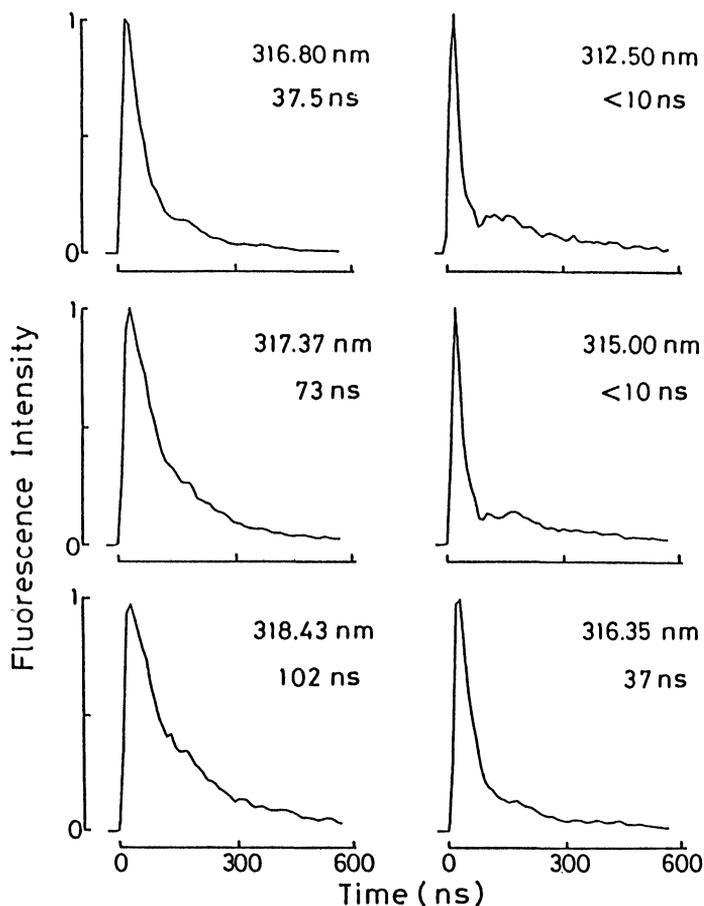
in fluorescence intensity (see Figure 3), whereas the threshold in CD<sub>3</sub>CDO could not be confirmed exactly from the excitation spectrum since the peak intensity rather gradually decreases with decreasing excitation wavelength in the region from 318 to 314 nm (see Figure 4).

In a bulk gas at room temperature, fluorescence decay with excitation at around the dissociation threshold shows a biexponential decay,<sup>11,20</sup> indicating that the intersystem crossing is reversible. The lifetime of the slow component under collision-free conditions has been shown in the bulk gas experiments to decrease nearly monotonically from 200 ns to 100 ns with decreasing excitation wavelength from 338.7 to 320 nm, and the slow component does not exist at excitation wavelengths below 315 nm.<sup>11</sup> Fluorescence decays in a jet observed at zero field with different excitation wavelengths across the dissociation threshold are shown in Figure 5. As reported by Noble and Lee,<sup>21,22</sup> fluorescence of CH<sub>3</sub>CHO observed in a jet shows a nearly single exponential decay with excitation into lower vibrational levels of S<sub>1</sub>. This is true even with excitation at 317.37 nm, which seems to prepare a vibrational level located near the dissociation threshold; the observed decay is well reproduced by assuming a single exponential decay with a lifetime of 73 ns, as is shown later.



**Figure 4** An expanded view of the fluorescence excitation spectrum of  $\text{CD}_3\text{CDO}$  at around 316 nm. Arrows indicate the excitation positions where fluorescence decays shown in Figures 6 were observed.

At excitation wavelengths below 317 nm, fluorescence decay observed in a jet cannot be reproduced by assuming a single exponential decay. At 316.80 nm, for example, a slowly decaying portion with a lifetime of about 200 ns exists besides the fast decaying portion with the lifetime of 37.5 ns. Note, however, that the slow component is very weak, as is seen in Figure 5. In the present jet experiments, a weak slowly-decaying portion exists even with excitation below 315 nm, as is seen in Figure 5, in contrast with the bulk gas experiments. The lifetime of the slow component is about 200 ns on any excitation below 317 nm. The result that this value is consistent with the lifetime of fluorescence emitted from lower vibronic levels of  $S_1$  seems not to be a mere accident. Further, the intensity of this component depends on the stagnation pressure. Then, we assign the slow component observed with excitation below 317 nm as the fluorescence emitted from lower vibrational levels of  $S_1$  of acetaldehyde produced by photodissociation of an acetaldehyde cluster formed in a jet, not as the fluorescence emitted from photoexcited levels of isolated molecules of acetaldehyde. In fact, a weak broad background, which may be assigned as the absorption of the cluster, exists at shorter wavelengths in the excitation spectrum (see Figure 1). If the slow component assigned as the emission originating



**Figure 5** Fluorescence decays of CH<sub>3</sub>CHO at zero field. Excitation positions are indicated in Figure 3 except for 315.0 and 312.5 nm excitations. The fluorescence lifetimes are shown in the figure.

from the cluster is neglected, the lifetime of the excited molecule prepared by photoexcitation is determined to be 102, 73, 37.5 and 37 ns at 318.43, 317.37, 316.80 and 316.35 nm, respectively. Below 315 nm, the lifetime is less than 10 ns and could not be determined in the present time resolution. Note that the lifetime in a jet varies from 98 to 220 ns at excitation wavelengths more than 320 nm.<sup>11,22</sup>

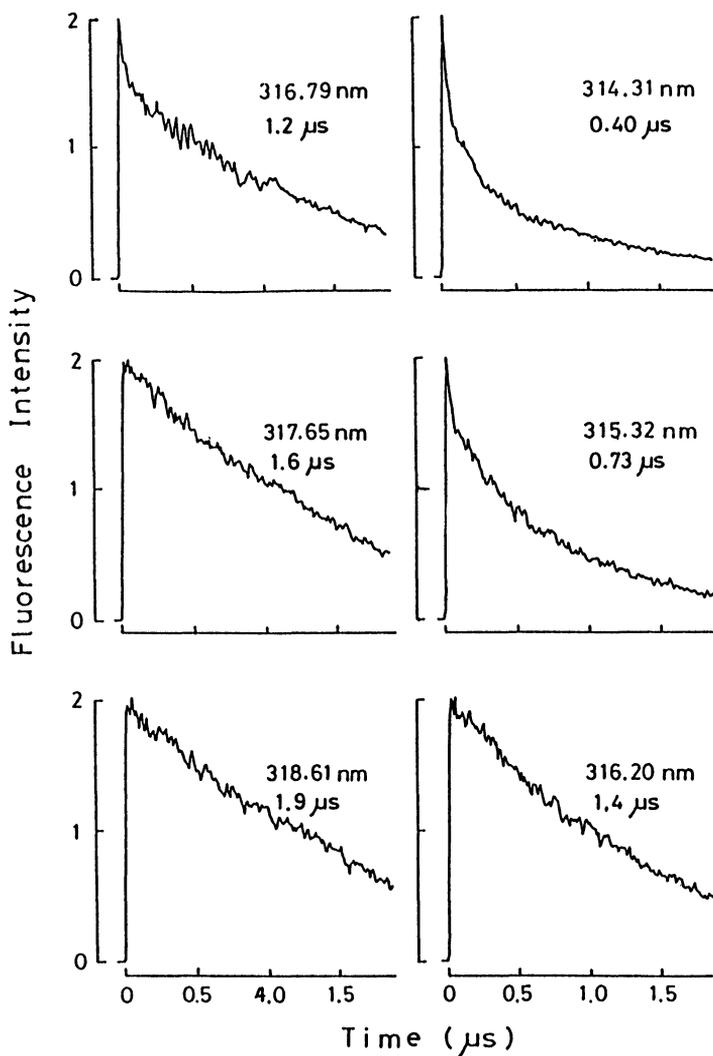
Fluorescence measurements in a bulk gas indicate that the fluorescence characteristics of CH<sub>3</sub>CHO belongs to the small molecule limit or intermediate case below the dissociation threshold and that the characteristics changes to the statistical limit above the threshold.<sup>11</sup> Accordingly, the lifetimes more than 37 ns mentioned above are assigned as the lifetimes of the slow component, whereas fluorescence having the lifetime of less than 10 ns for excitation below 315 nm may be assigned as the fast component characterized by the statistical limit, where the lifetime corresponds to the energy width in which the singlet-triplet mixed states are distributed. This

suggests that the fluorescence characteristics changes from the small molecule limit to the statistical limit across the dissociation threshold. The biexponential decay observed in a bulk gas could not be observed at zero field for fluorescence of jet-cooled  $\text{CH}_3\text{CHO}$ , suggesting that higher rotational levels and/or internal rotor levels located near the dissociation threshold neither of which can be prepared in the jet exhibit the intermediate case behavior of fluorescence at zero field.

Fluorescence of  $\text{CD}_3\text{CDO}$  at zero field also shows a nearly single exponential decay with excitation at wavelengths more than 317 nm. As is shown in Figure 6, for example, fluorescence following excitation at 318.61 and 317.65 nm shows a single exponential decay with a lifetime of 1.9 and 1.6  $\mu\text{s}$ , respectively. At wavelengths less than 317 nm, however, fluorescence shows a nonexponential decay. At 316.79 nm excitation, for example, the decay can be analyzed by assuming a biexponential decay; the decay profile of the fast component is consistent with the time profile of the excitation light and the slow component has a lifetime of 1.2  $\mu\text{s}$ . Note that all the decays at excitation wavelengths less than 317 nm are not nonexponential, e.g., fluorescence for 316.2 nm excitation shows a single exponential decay (Figure 6). At excitation wavelengths less than 316 nm, fluorescence decay can be roughly reproduced by assuming a tri-exponential decay. The decay profile of the fast component is identical with the shape of the excitation light. The initially decaying portion of the slow component markedly depends on the excitation wavelength, and its lifetime is evaluated to be 0.73 and 0.40  $\mu\text{s}$  at 315.32 and 314.31 nm, respectively. These lifetimes as well as the lifetimes of the slow component at other excitation positions are considered to correspond to the energy width of the individual mixed states composed of the zero-order  $S_1$  state and zero-order triplet states coupled to  $S_1$ . Roughly speaking, these lifetimes may be regarded as the lifetimes of the triplet states coupled to  $S_1$ . Then, the marked decrease of the lifetime of the slow component at wavelengths less than 317 nm with increasing excitation energy suggests that the dissociation rate abruptly increases with increasing excitation energy since the photodissociation occurs through the triplet state. At excitation wavelengths less than 317 nm, further, a fast dephasing decay is observed following excitation into  $S_1$  of  $\text{CD}_3\text{CDO}$  probably because the photodissociation through the triplet states plays a role to increase the level density of the triplet state coupled to  $S_1$ . At excitation wavelengths below 316 nm, the other slow component with a lifetime of  $\sim 2 \mu\text{s}$  exists. This component may be assigned as the fluorescence emitted from lower vibronic levels of  $S_1$  of  $\text{CD}_3\text{CDO}$  produced by photodissociation of a cluster, as in the case of  $\text{CH}_3\text{CHO}$ . In fact, a broad background, which seems to be assigned as the absorption of the cluster of  $\text{CD}_3\text{CDO}$ , is noticed at shorter wavelengths in the excitation spectrum shown in Figure 2.

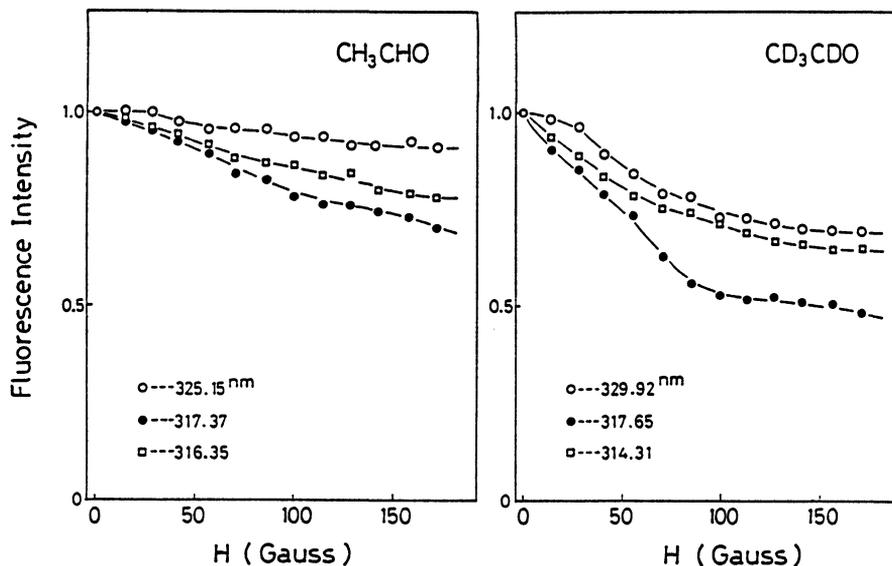
### 3.2. Magnetic field effects on fluorescence

Fluorescence of acetaldehyde vapor is quenched by  $H$ . Plots of the fluorescence intensity integrated over the full decay of  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{CDO}$  are shown in Figure 7 as a function of  $H$  at different excitation wavelengths. At all the excitations examined in the region from 330 to 310 nm, fluorescence intensity of both com-



**Figure 6** Fluorescence decays of CD<sub>3</sub>CDO at zero field. Excitation positions are indicated in Figure 4. The lifetime of the initially decaying portion of the slow fluorescence is shown in the figure.

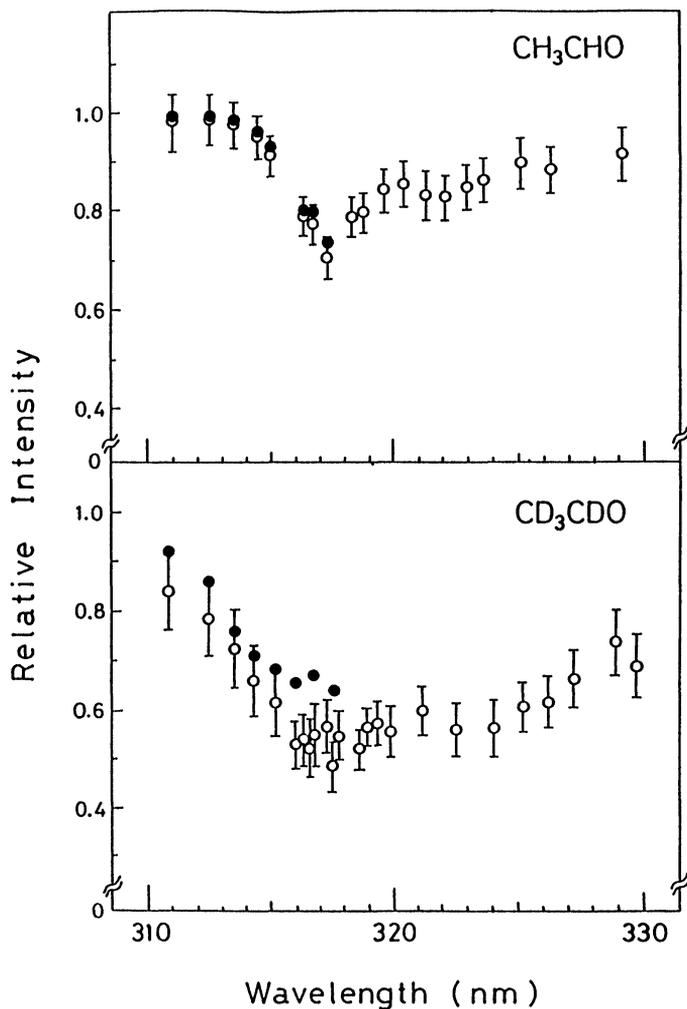
pounds monotonically decreases with increasing  $H$ , and the quenching by  $H$  depends on the excitation wavelength. The fluorescence intensity at 170 G relative to the zero-field intensity, denoted by  $I_f(170)$ , was obtained for various excitation positions in the region from 330 to 310 nm. All the excitation positions examined are indicated by a vertical line in Figures 1 and 2. Plots of  $I_f(170)$  as a function of excitation wavelength are shown in Figure 8. Note that a distinct absorption band could not be excited at excitation wavelengths less than 315 and 314 nm in CH<sub>3</sub>CHO and CD<sub>3</sub>CDO, respectively, since a distinct peak could not be resolved in this region. At



**Figure 7** Plots of the fluorescence intensity of  $\text{CH}_3\text{CHO}$  (left) and  $\text{CD}_3\text{CDO}$  (right) as a function of  $H$ . Excitation wavelengths are shown in the figure.

shorter excitation wavelengths, fluorescence originating from the photodissociation of a cluster seems to overlap the fluorescence of photoexcited acetaldehyde under consideration, as mentioned previously. In order to reduce the contribution of the former fluorescence, which must be excluded to examine the excitation energy dependence of the magnetic quenching of fluorescence under consideration especially above the dissociation threshold,  $I_f(170)$  was obtained also by integrating the decay from 0 to 200 ns in both compounds. The results are shown in Figure 8 for excitation wavelengths less than 317.5 and 318 nm in  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{CDO}$ , respectively, together with the results obtained by integrating the full decay.

As is shown in Figure 8,  $(1 - I_f(170))$  in  $\text{CD}_3\text{CDO}$  is larger than that in  $\text{CH}_3\text{CHO}$  by a factor of about 2 at each excitation wavelength more than 316 nm, indicating that the efficiency of magnetic quenching is higher in  $\text{CD}_3\text{CDO}$  than in  $\text{CH}_3\text{CHO}$ . It is also found that the efficiency of magnetic quenching nearly monotonically increases with decreasing excitation wavelength in the region more than 317 and 316 nm in  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{CDO}$ , respectively. When the plots are examined carefully, however, a fluctuation exists for  $I_f(170)$ , i.e., a local maximum is seen at around 321 nm and at 329 nm in  $\text{CD}_3\text{CDO}$ . As is shown in Figure 8, further, the excitation wavelength dependence of magnetic quenching of fluorescence drastically changes at around 317 and 316 nm in  $\text{CH}_3\text{CHO}$  and  $\text{CD}_3\text{CDO}$ , respectively, where dissociation threshold is considered to be located, i.e., the magnetic quenching becomes less efficient with decreasing excitation wavelength beyond these wavelengths. Thus, not only the fluorescence property at zero field but also the magnetic field effects on fluorescence property drastically change across the dissociation threshold. Above the dissociation threshold, further, the magnetic quenching

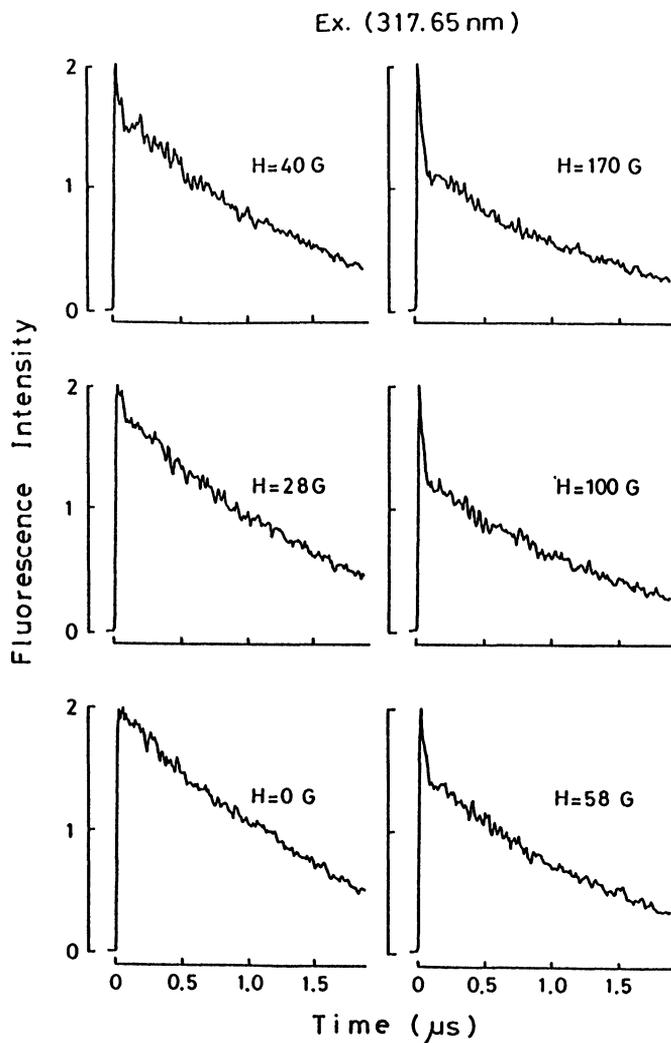


**Figure 8** Plots of the fluorescence intensity at 170 G relative to the intensity at zero field as a function of excitation wavelength for CH<sub>3</sub>CHO (upper) and CD<sub>3</sub>CDO (lower): (○), the intensity was obtained by integrating the full decay; (●), the intensity was obtained by integrating the decay from 0 to 200 ns.

becomes less efficient more rapidly in CH<sub>3</sub>CHO than in CD<sub>3</sub>CDO, as the excitation energy increases. The change of the fluorescence characteristics at zero field across the dissociation threshold also is more drastic in CH<sub>3</sub>CHO than in CD<sub>3</sub>CDO. In fact, the dissociation threshold of CH<sub>3</sub>CHO is estimated to be at 317.25 nm from the sudden drop in intensity, whereas the photodissociation threshold of CD<sub>3</sub>CDO could not be confirmed from the fluorescence excitation spectrum even in a jet since the peak intensity of the spectrum gradually decreases with decreasing excitation wavelength in the region from 318 to 314 nm, as mentioned previously. From the excitation energy dependence both in decay profile at zero field and in efficiency of

magnetic quenching, however, the dissociation threshold of  $\text{CD}_3\text{CDO}$  may be regarded as located in the region of 316–317 nm.

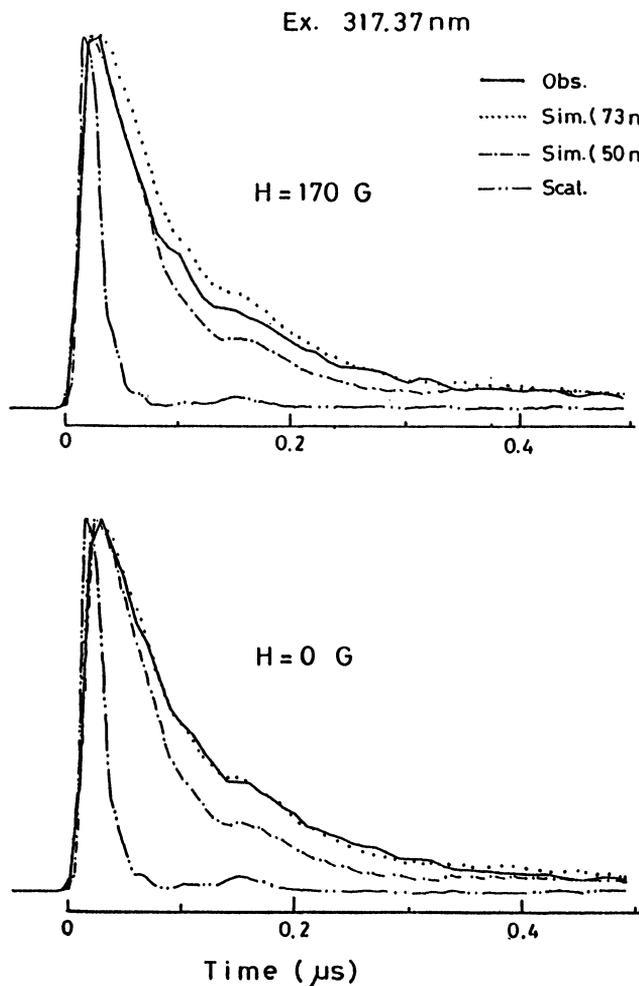
Fluorescence decay profiles are also affected by  $H$  in both compounds. Fluorescence decay profiles of  $\text{CD}_3\text{CDO}$  at different strengths of  $H$  are shown in Figure 9 for 317.65 nm excitation. As  $H$  increases, a single exponential decay changes to a biexponential, and the intensity of the fast component relative to the slow one increases. When fluorescence shows a nonexponential decay at zero field, e.g., at 316.79 or 315.32 nm excitation (see Figure 6), the intensity of the fast component relative to the slow one increases with increasing  $H$ . At excitation wavelengths longer



**Figure 9** Magnetic field dependence of the fluorescence decay profile of  $\text{CD}_3\text{CDO}$  with excitation at 317.65 nm.

than 325 nm, however, fluorescence of CD<sub>3</sub>CDO still shows a single exponential decay even when  $H$  is raised up to 170 G.

Fluorescence decay of CH<sub>3</sub>CHO at 170 G on excitation at 317.37 nm is shown in Figure 10, together with the decay at zero field. As mentioned previously, the decay profile at zero field is well reproduced by assuming a single exponential decay with a lifetime of 73 ns. On the other hand, the decay profile at 170 G cannot be reproduced by assuming a single exponential decay; the lifetime of the slowly decaying portion seems to be the same as that at zero field, whereas the decay of the initial portion becomes faster with increasing  $H$ , i.e. about 50 ns at 170 G, as is



**Figure 10** Fluorescence decay profile of CH<sub>3</sub>CHO at zero field (lower) and at 170 G (upper) with excitation at 317.37 nm: (—), observed decay; (···), simulated by assuming a single exponential decay with a lifetime of 73 ns; (- - -), simulated by assuming a single exponential decay with a lifetime of 50 ns; (- · -), decay profile of the scattered light.

shown in Figure 10. This result indicates that the fluorescence decay of  $\text{CH}_3\text{CHO}$  also becomes biexponential in the presence of  $H$ . At excitation wavelengths below 315 nm, however, the decay profile is nearly unaffected by  $H$  except for a slight quenching of the slow component which is assigned to the fluorescence originating from a cluster, suggesting that the fast component of fluorescence characterized by the statistical limit is unaffected by  $H$ .

The field-induced change from a single exponential decay to a biexponential one suggests that the number of levels in the triplet state coupled to  $S_1$  ( $N_{\text{eff}}$ ) increases with increasing  $H$ .<sup>5-7</sup> Then, the magnetic quenching of fluorescence is attributed to an increase of  $N_{\text{eff}}$  by  $H$ , as in the case of some azaaromatic molecules. Thus, the magnetic field effects on fluorescence property for excitation below the dissociation threshold are well understood by assuming that  $N_{\text{eff}}$  is increased by  $H$ . As mentioned above, the efficiency of magnetic quenching becomes higher with increasing excitation energy and the efficiency is much higher in  $\text{CD}_3\text{CDO}$  than in  $\text{CH}_3\text{CHO}$  with excitation below the dissociation threshold. Both results indicate that the efficiency of magnetic quenching is related to the level density of the triplet state coupled to  $S_1$ ; the efficiency becomes higher with increasing the level density of the triplet state coupled to  $S_1$ .

The presence of the fast component of fluorescence at zero field in  $\text{CD}_3\text{CDO}$  at excitation wavelengths less than 317 nm may be attributed to the presence of dissociation via higher vibrational levels of  $T_1$ , which leads to an abrupt increase of  $N_{\text{eff}}$ . The decrease of the lifetime of the slow component of fluorescence with decreasing excitation wavelength below 317 nm in both compounds implies that the dissociation rate at the triplet state markedly increases with increasing excess energy. The slow component of fluorescence is quenched by  $H$ , suggesting that  $H$  as well as dissociation via triplet states leads to an increase of  $N_{\text{eff}}$ . On the contrary, the fast component shows inefficient magnetic field effects. As a result, the magnetic quenching becomes less efficient with increasing excess energy above the dissociation threshold since the fast component relative to the slow one abruptly increases with increasing excess energy. Fluorescence of  $\text{CD}_3\text{CDO}$  for 316.79 nm excitation shows a biexponential decay even at zero field, whereas fluorescence at 316.20 nm excitation shows a single exponential decay, as is shown in Figure 6. Further, the lifetime of the slow component at the former excitation ( $1.2 \mu\text{s}$ ) is shorter than the latter ( $1.4 \mu\text{s}$ ). These results imply that the dissociation following 316.79 nm excitation is faster than that following 316.20 nm excitation, though the levels prepared by the latter excitation are considered to have more excess energy than the former. Strictly speaking, therefore, it seems that the dissociation rate does not increase monotonically with increasing excess energy but shows a mode specificity.

Hanazaki and co-workers<sup>14</sup> measured the photofragment excitation spectrum for the photochemical reaction of  $\text{CH}_3\text{CHO}$  by monitoring the  $\text{HCO}$  radical. They have shown that  $\text{HCO}$  signal is detected with the excitation wavelengths up to 320.5 nm, implying that 320.5 nm is the dissociation threshold in  $\text{CH}_3\text{CHO}$ . Thus, the threshold determined by the excitation energy dependence of the fluorescence properties, i.e., 317.25 nm, disagrees with the one determined by the photofragment spectrum, i.e., 320.5 nm. The result of the photofragment spectrum is rather strange since the fluorescence property

and its magnetic field effects in CH<sub>3</sub>CHO show no indication of photodissociation at excitation wavelengths more than 318 nm. Hanazaki and co-workers have proposed that this discrepancy comes from the excess energy dependence of the dissociation rate, by employing the Kassel model. However, this discrepancy seems to still remain unsettled. The fact that the lifetime of the slow fluorescence is shorter in CH<sub>3</sub>CHO than in CD<sub>3</sub>CDO across the dissociation threshold implies that the dissociation rate at the triplet state is faster in CH<sub>3</sub>CHO than in CD<sub>3</sub>CDO at the same excitation wavelength. Further, the present results imply that the excess energy dependence of the dissociation rate is more drastic in CH<sub>3</sub>CHO than in CD<sub>3</sub>CDO, as mentioned previously. These deuterium effects seem to suggest that a kind of tunneling process participates in the dissociation process. In order to elucidate the mechanism of the dissociation process of acetaldehyde vapor and interpret the discrepancy between the results obtained from the fluorescence measurement and the photofragment measurement, a comparison between the fluorescence excitation spectrum and the photofragment excitation spectrum not only in CH<sub>3</sub>CHO but also in its deuterated compounds may be useful. A comparison between the fluorescence excitation spectrum and the photofragment excitation spectrum in the presence of *H* also seems to give a very important information concerning these problems.

#### 4. CONCLUSION

Fluorescence property as well as its magnetic field dependence in acetaldehyde vapor in a jet drastically changes across the excitation wavelength of about 317 nm; the fluorescence intensity as well as the efficiency of magnetic quenching of fluorescence abruptly decreases with decreasing excitation wavelength beyond this wavelength. The sudden change is attributed to the photodissociation following excitation into S<sub>1</sub>, and the dissociation is considered to occur via the triplet states following intersystem crossing from S<sub>1</sub>. *H* as well as the dissociation plays a role to increase the level density of the triplet state coupled to S<sub>1</sub>. The dissociation threshold is estimated to be at 317.25 nm in CH<sub>3</sub>CHO and at around 316–317 nm in CD<sub>3</sub>CDO, based on the excitation energy dependence of the fluorescence property and its magnetic field dependence. The present threshold of CH<sub>3</sub>CHO is quite different from the one determined by the photofragmentation experiments, i.e., 320.5 nm in CH<sub>3</sub>CHO, and this inconsistency still remains unsettled. The dissociation rate is suggested to become faster with increasing excess energy above the dissociation threshold both in CH<sub>3</sub>CHO and in CD<sub>3</sub>CDO, but CD<sub>3</sub>CDO seems to show a rather slow excess energy dependence, in comparison with CH<sub>3</sub>CHO.

#### *Acknowledgements*

These experiments were carried out at the Research Institute of Applied Electricity (currently Research Institute for Electronic Science) at Hokkaido University. The author thanks professors T. Takemura and I. Suzuka for their help during the experiments and Mr. T. Koguchi for his experimental assistance. This work was partly

supported by a Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No. 228/04242107) from the Ministry of Education, Science and Culture, Japan.

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