

THE C=O STRETCHING FREQUENCY IN THE S₁($\pi^* - n$) STATE OF ACETALDEHYDE AND ITS DEUTERATED DERIVATIVES DETERMINED WITH THE PHOTOFRAGMENT EXCITATION SPECTROSCOPY

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(Received 15 April, 1994)

The vibrational structure was recorded for the S₁($\pi^* - n$) state of acetaldehyde (CH₃CHO) and its deuterated derivatives (CH₃CDO, CD₃CHO and CD₃CDO) up to ~3500 cm⁻¹ above the 0–0 bands with the LIF (laser induced fluorescence) and PHOFEX (photofragment excitation) techniques. In the PHOFEX spectroscopy, the yield of the formyl radical, HCO(\bar{X}) or DCO(\bar{X}), produced in the photodissociation of acetaldehyde is measured against the excitation frequency. The yield was determined by monitoring one of the rotational lines in the $\tilde{B} \leftarrow \tilde{X}$ transition of the formyl radical by the LIF technique. This is the first measurement of the vibronic structure of acetaldehydes in supersonic jets above the dissociation threshold where they are non-fluorescent. The results have made it possible to locate ν_4 (the C=O stretching) and $2\nu_4$ bands unequivocally; the ν_4 fundamentals at 1217, 1189, 1210 and 1178 cm⁻¹ above the 0–0 band for CH₃CHO, CH₃CDO, CD₃CHO and CD₃CDO, respectively. The corresponding overtone ($2\nu_4$) bands are observed, respectively, at 2414, 2350, 2399 and 2334 cm⁻¹. All the vibronic bands newly observed in the PHOFEX spectra are found to be interpreted as the combinations of ν_4 and $2\nu_4$ with the modes appearing in the lower frequency (< 1200 cm⁻¹) region, which consist of ν_{10} (the C—C—O in-plane bending), ν_{14} (the C=O out-of-plane wagging) and ν_{15} (the methyl torsion).

KEY WORDS: Acetaldehyde; LIF; PHOFEX; vibronic structure.

1. INTRODUCTION

The spectroscopy and dynamics of acetaldehyde in the gas phase have been studied extensively, since it is considered to be one of the typical carbonyl compounds whose photochemical behaviour attracts profound interest.¹ Recently, we have reported detailed studies on the photodissociation of jet-cooled acetaldehyde in the lowest excited singlet electronic (S₁) state,^{2–4} where the rotational and vibrational excitation of the product, HCO, have been determined as a function of dissociating photon

energy. The threshold for the appearance of HCO has also been determined. The rotational excitation of HCO was found to be determined solely by the energy released at the exit channel below the barrier,³ while the vibrational excitation is determined by the excess energy above the reaction barrier.⁴

The vibronic structure in the $S_1(\pi^* - n)$ state of acetaldehyde has long attracted interests in relation to the structural change accompanying the $\pi^* \leftarrow n$ transition and also to possible mode selective dynamics.⁵ In spite of intensive investigations, the vibronic assignment is still incomplete; in the early assignments performed for the electronic-absorption or LIF (laser induced fluorescence) spectra measured at room temperature,⁶⁻⁸ the 0–0 band was misassigned because of the spectral congestion due to the hot species. The location of the 0–0 band was definitely fixed later in the highly resolved LIF-excitation spectra measured for jet-cooled acetaldehyde. It has been found that most of the vibronic bands appearing up to 1000 cm^{-1} from the 0–0 band are assigned to the fundamental, overtone and combination bands of the ν_{10} (the in-plane C—C—O bending), ν_{14} (the C=O out-of-plane wagging) and ν_{15} (the methyl torsion) modes.^{5,9-11}

The frequency of the ν_4 (the C=O stretching) mode in S_1 is of particular interest, since its frequency is expected to decrease drastically from the ground-state value because of the occupation of the π^* bond. It is also expected that the ν_4 mode is Franck-Condon active because of the change in the C=O bond length upon the electronic excitation.^{8,10,12,13} Noble *et al.*,¹⁰ however, failed in assigning the 4_0^1 band because of considerable band congestion even under the supersonic jet condition. Baba *et al.*¹¹ tentatively assigned the 1173 and 1119 cm^{-1} bands of CH_3CHO and CH_3CDO , respectively, to the ν_4 mode on the basis of the analogy with formaldehyde and cyclic ketones.

The electronic excitation of CH_3CHO above $0_0^0 + 1420\text{ cm}^{-1}$ causes the dissociation into HCO and CH_3 , which quenches the fluorescence.² Therefore, only the vibronic structure below $\sim 1800\text{ cm}^{-1}$ can be measured by the LIF technique. This is one of the reasons which make the definite assignment of the C=O stretching band difficult.

Recently, we found the PHOFEX (photofragment excitation) spectroscopy to be useful in obtaining information on the vibronic structure of acetaldehyde above the dissociation threshold.² In this scheme, the formyl radical (HCO or DCO) in the ground electronic state, which is one of the dissociation products, is monitored by the LIF technique with a delayed probe pulse. The formyl radical can be probed sensitively by employing its $\tilde{B} \leftarrow \tilde{X}$ transition.¹⁴⁻¹⁶ Excitation spectra of acetaldehyde are obtained by measuring the yield of the formyl radical against the pump frequency. In this paper, we present the PHOFEX spectra of acetaldehyde and the deuterated derivatives (CH_3CDO , CD_3CHO and CD_3CDO) in supersonic jets up to $\sim 3500\text{ cm}^{-1}$ above the 0–0 band. The spectra are analyzed together with the LIF-excitation spectra with particular emphasis on the determination of the vibronic band due to the ν_4 mode.

2. EXPERIMENTAL

The LIF-excitation spectra of acetaldehyde were measured with the frequency-doubled output of a dye laser (Quantel: TDL-50, 0.5~1 mJ/pulse, line width: 0.2~0.5 cm⁻¹) pumped by the second harmonics of a Nd:YAG laser (Quantel: YG571C). The same laser operated with the higher output power (1.5~3 mJ/pulse) was used as the pump laser for the PHOFEX measurements. The frequency of the laser was calibrated with a “see-through” hollow cathode lamp (Hamamatsu: L2783-13-NE-AL). The probe source for the PHOFEX measurements was an excimer-laser-pumped dye laser (Lumonics: HE-420-SM-B and Lambda Physik: FL3002, ~0.8 mJ/pulse, line width: ~0.2 cm⁻¹). The probe frequency was set at one of the rotational lines of the formyl radical (HCO or DCO) in the 0–0 band of the $\tilde{B} \leftarrow \tilde{X}$ transition.

The laser beams were aligned almost collinearly, and focused onto the molecular beam 16 mm downstream from the nozzle exit. Total emission from acetaldehyde or the formyl radical was collected onto a photomultiplier (Hamamatsu: R955), whose output was integrated by a boxcar averaging system (Stanford Research Systems: SR235, SR240, SR243 and SR250). In the LIF measurements, the gate (100 ns) of the boxcar was opened 50 ns after the excitation pulse. In the PHOFEX measurements, the delay between the pump and probe pulses was 1 μ s with the 70 ns gate opened simultaneously with the probe pulse. In the PHOFEX measurements, a band-path filter (HOYA: U-330) was used in front of the photomultiplier to eliminate the scattering of the laser pulses.

Helium containing ca. 5% acetaldehyde was expanded into a vacuum chamber from a conventional pulsed valve with a 0.8-mm-diameter orifice. Acetaldehydes [CH₃CHO (Merck, > 99.5%), CH₃CDO (MSD isotope, 97 atom % D), CD₃CHO (MSD isotope, 98.3 atom % D) and CD₃CDO (Aldrich, 99+ atom % D)] were used without further purification. The stagnation pressure of the gas mixture was 2.2 atm. The background pressure in the chamber was held below 10⁻⁴ Torr during the measurements.

3. RESULTS AND DISCUSSION

Figure 1 shows the (a) LIF-excitation and (b) PHOFEX spectra of CH₃CHO in a supersonic jet obtained by pumping the $S_1(\pi^* - n, \tilde{\lambda})$ state. The ordinate shows the frequency shift from the 0–0 band at 29769 cm⁻¹ ($\equiv 0\%$). These spectra are not calibrated for the pump power, which varied by a factor of about 2. The band intensities can, therefore, be discussed only qualitatively. The LIF-excitation spectrum is in agreement with the spectra reported previously.⁹⁻¹¹ No hot band is observed in the energy region lower than the 0–0 band.

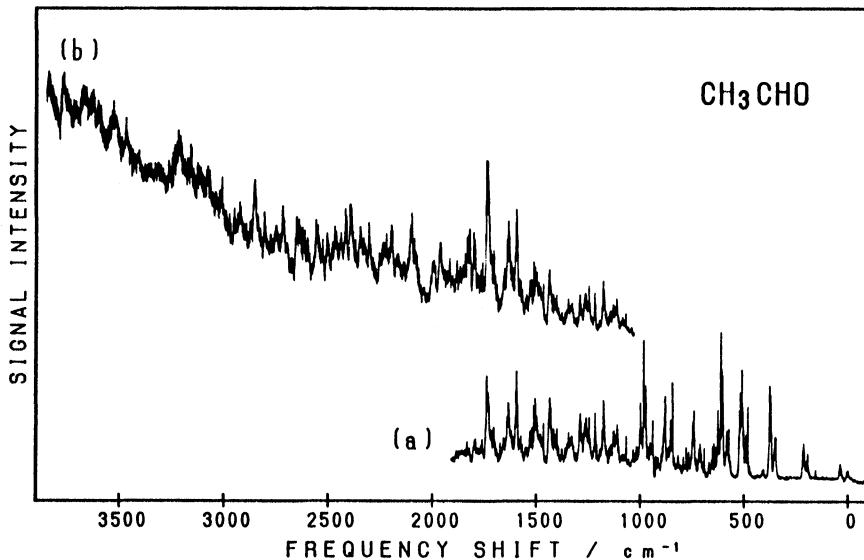


Figure 1 (a) LIF-excitation and (b) PHOFEX spectra of CH_3CHO in a supersonic jet. The ordinate shows the frequency shift from the 0–0 band at 29769 cm^{-1} .

The fluorescence from CH_3CHO is observed only for the excitation frequencies lower than $0_0^0 + 1835 \text{ cm}^{-1}$, above which it disappears because of the opening of the dissociation channel to HCO and CH_3 . Therefore, vibronic structure of acetaldehyde in the higher frequency region cannot be measured by the LIF technique. A few spectroscopic techniques have been proposed to measure the excitation spectra of the non-fluorescent compounds. Among them, the hole-burning spectroscopy (pump-probe absorption depletion spectroscopy)^{17–19} and the REMPI (resonance enhanced multiphoton ionization) technique^{20,21} seem to be difficult to be applied to acetaldehyde because of small cross sections of the vibronic transitions and the fast intersystem crossing for the higher vibrational levels in S_1 . On the other hand, the PHOFEX spectroscopy is applicable, in which one of the dissociation products, formalyl radical, is probed sensitively with the LIF technique employing the $\tilde{\text{B}} \leftarrow \tilde{\text{X}}$ transition.^{2,14,16}

The PHOFEX spectrum in Figure 1 was measured by setting the probe frequency at a rotational line in the 0–0 band of the HCO $\tilde{\text{B}} \leftarrow \tilde{\text{X}}$ transition. The rotational line employed is indicated in the LIF-excitation spectrum of HCO shown in Figure 2a. The bands appearing in the PHOFEX spectrum below the onset of the fluorescence ($< 0_0^0 + 1835 \text{ cm}^{-1}$) are at least partly due to the long tails of fluorescence which could not be removed completely even with the delay of $1 \mu\text{s}$ between the pump and probe pulses. This, however, would not bring about any serious difficulty in the vibronic assignments.

Figure 3 shows the spectra for CD_3CHO similar to Figure 1. The spectra for CH_3CDO and CD_3CDO are shown, respectively, in Figures 4 and 5, where PHOFEX spectra are measured by monitoring DCO . The LIF-excitation spectra of DCO is

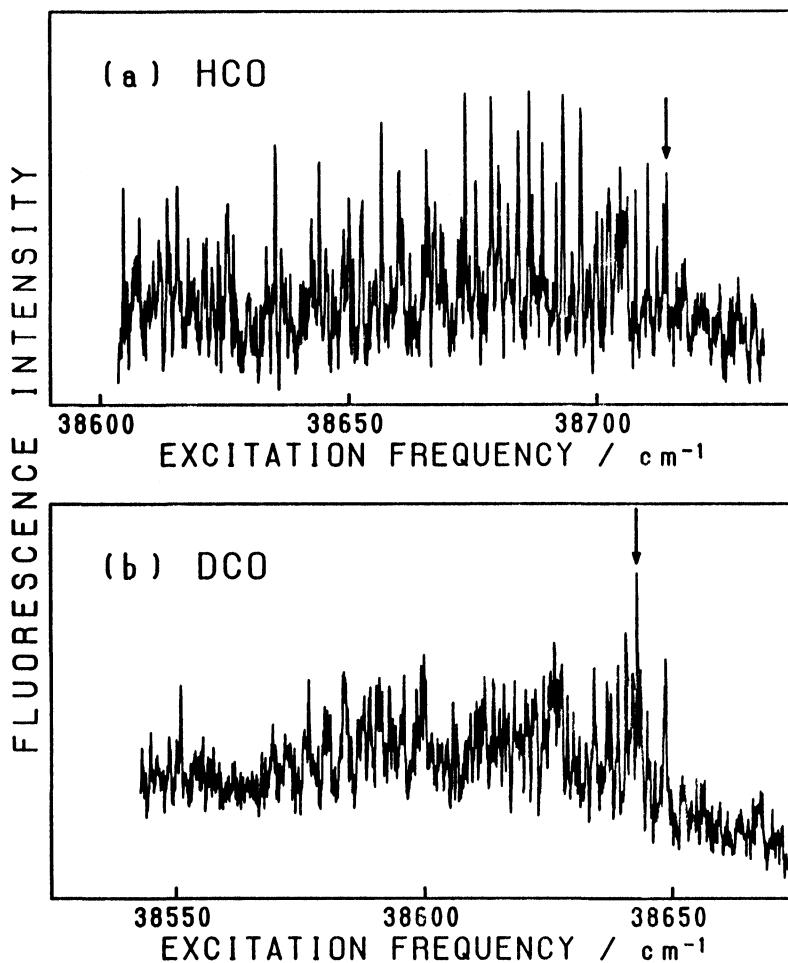


Figure 2 LIF-excitation spectrum of (a) HCO and (b) DCO. The rotational lines used for the PHOFEX measurements are indicated by an arrow.

shown in Figure 2b, where the rotational line used in the PHOFEX measurements is indicated. Inspection of these spectra gives us an insight that almost all the vibronic band observed for these four isotope species can be assigned to the repetition of the same vibronic structure starting at 0_0^0 , 4_1^1 and 4_0^2 .

The ν_4 mode is expected to be Franck-Condon active in the excitation spectrum of acetaldehyde.^{8,11} It has been pointed out that one of the bands around $0_0^0 + 1200 \text{ cm}^{-1}$ should correspond to the ν_4 mode.^{10,11} To facilitate the assignment, the CD_3CDO spectra are rearranged as illustrated in Figure 6, where (a) is the excitation spectrum synthesized from the LIF-excitation and PHOFEX spectra shown in Figure 5. Figure 6b is the same as the lower energy part ($< 2000 \text{ cm}^{-1}$) of (a) shifted to the higher energy by 1178 cm^{-1} . In (b), the bands assigned to those belonging to the progression starting from the 0_0^0 are shaded. The corresponding

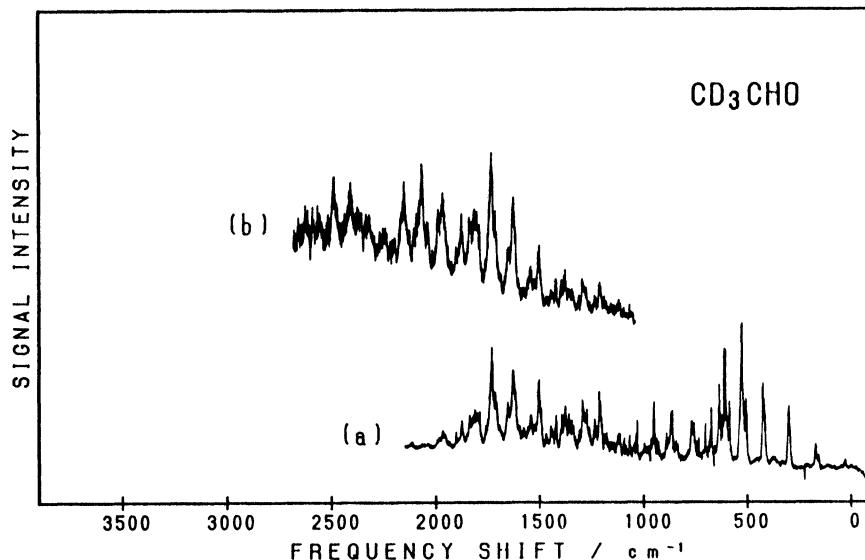


Figure 3 (a) LIF-excitation and (b) PHOFEX spectra of CD_3CHO in a supersonic jet. The ordinate shows the frequency shift from the 0–0 band at 29759 cm^{-1} .

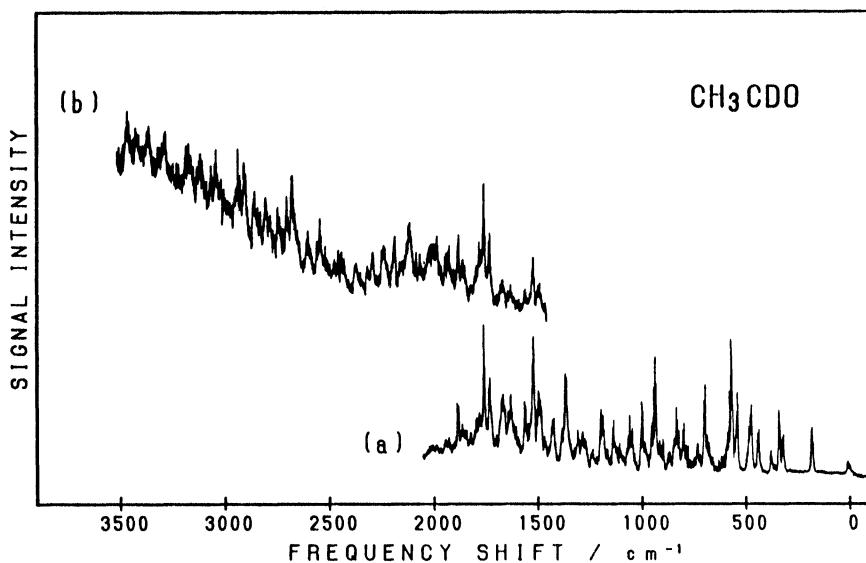


Figure 4 (a) LIF-excitation and (b) PHOFEX spectra of CH_3CDO in a supersonic jet. The ordinate shows the frequency shift from the 0–0 band at 29825 cm^{-1} .

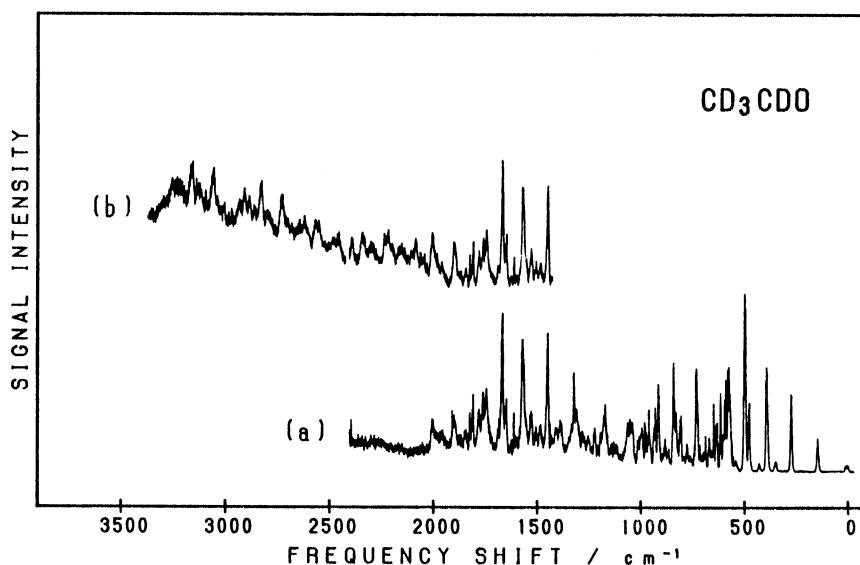


Figure 5 (a) LIF-excitation and (b) PHOFEX spectra of CD_3CDO in a supersonic jet. The ordinate shows the frequency shift from the 0–0 band at 29810 cm^{-1} .

bands in (a) are shaded to facilitate the comparison. It is seen that the shaded bands in (a) can be assigned perfectly as the repetition of the bands starting at 0_0^0 [shaded in (b) below 1600 cm^{-1}]. The non-shaded bands in (a) above 2300 cm^{-1} corresponds well to (c), which is again the repetition of (a) starting at 2334 cm^{-1} . We assigned the 1178 and 2334 cm^{-1} bands to 4_0^1 and 4_0^2 , respectively. It is to be noted that the assignment of 4_0^1 and 4_0^2 is unequivocal, since the characteristic feature in the 0 – 500 cm^{-1} region due to the ν_{15} methyl torsional mode is repeated from the 4_0^1 and 4_0^2 bands; no reasonable assignment of all the observed bands is possible if one shifts the frequency of 4_0^1 or 4_0^2 . Similar analyses are given in Figures 7–9 for CH_3CHO , CD_3CHO and CH_3CDO . In each case, all observed vibronic bands can be assigned as to be the combinations of the lower-energy bands with 4_0^1 and 4_0^2 .

The frequencies of ν_4 and $2\nu_4$ observed for normal and deuterated acetaldehydes are summarized in Table 1, together with the frequencies of their 0–0 transitions and parameters A and B in the Birge-Sponer plot:²²

Table 1 Frequencies of the C=O stretching mode for acetaldehyde and its deuterated derivatives.^{a)}

	$0/\text{cm}^{-1}$	ν/cm^{-1}	$2\nu/\text{cm}^{-1}$	A/cm^{-1}	B/cm^{-1}
CH_3CHO	29769	1217	2414	1227	-10
CH_3CDO	29825	1189	2350	1203	-14
CD_3CHO	29759	1210	2399	1221	-11
CD_3CDO	29810	1178	2334	1189	-11

a) A and B are the Birge-Sponer coefficients; $\tilde{\nu}/n = A + Bn$, where $\tilde{\nu}$ is the frequency and n is the quantum number.

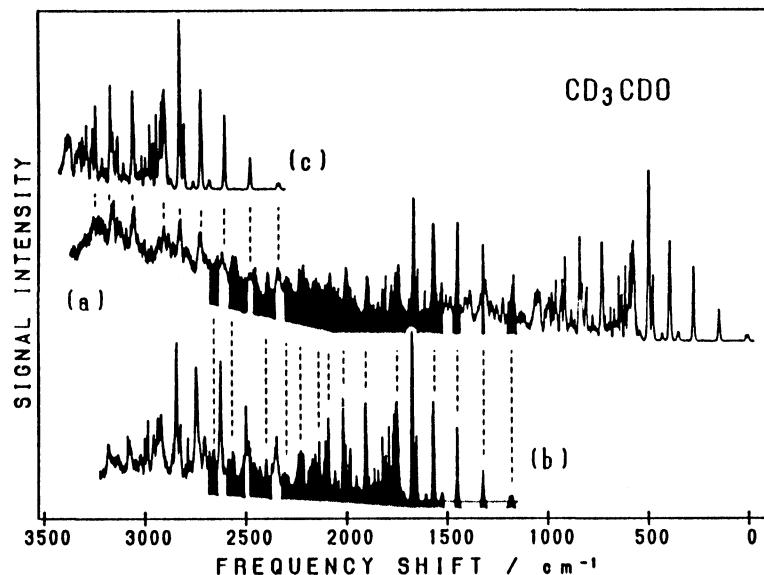


Figure 6 (a) Excitation spectrum of CD_3CDO synthesized from the LIF-excitation and PHOFEX spectra shown in Figure 5. (b) The same spectrum as (a) shifted by ν_4 (1178 cm^{-1}) to the higher energy. (c) same spectrum as (a) shifted by $2\nu_4$ (2334 cm^{-1}). Shaded bands in (b) belong to 0_0^0 , while those shaded in (a) belongs to 4_0^1 .

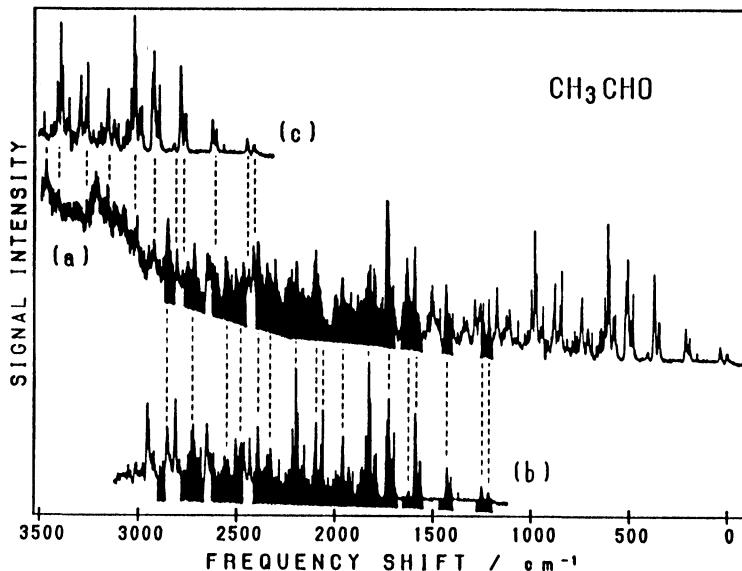


Figure 7 (a) Excitation spectrum of CH_3CHO synthesized from the LIF-excitation and PHOFEX spectra shown in Figure 1. (b) The same spectrum as (a) shifted by ν_4 (1217 cm^{-1}) to the higher energy. (c) The same spectrum as (a) shifted by $2\nu_4$ (2414 cm^{-1}). Shaded bands in (b) belong to 0_0^0 , while those shaded in (a) belongs to 4_0^1 .

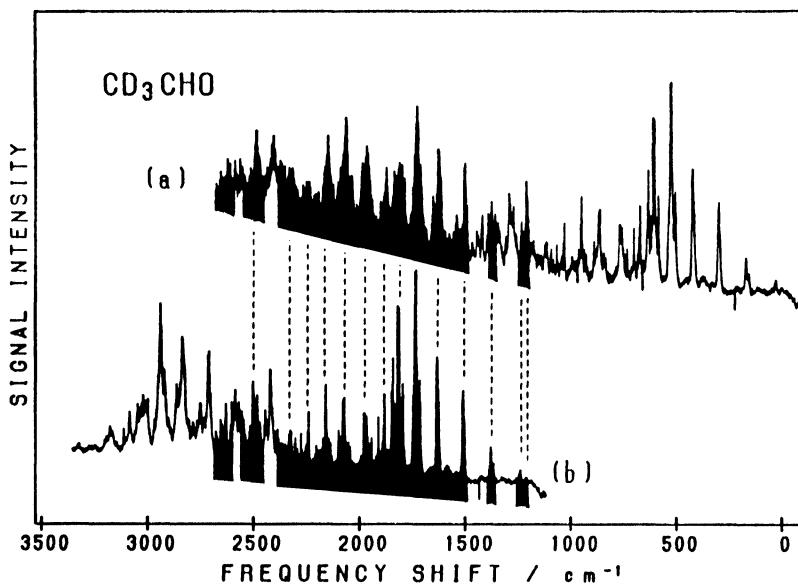


Figure 8 (a) Excitation spectrum of CD_3CHO synthesized from the LIF-excitation and PHOFEX spectra shown in Figure 3. (b) The same spectrum as (a) shifted by ν_4 (1210 cm^{-1}) to the higher energy. (c) The same spectrum as (a) shifted by $2\nu_4$ (2399 cm^{-1}). Shaded bands in (b) belong to 0_0^0 , while those shaded in (a) belongs to 4_0^1 .

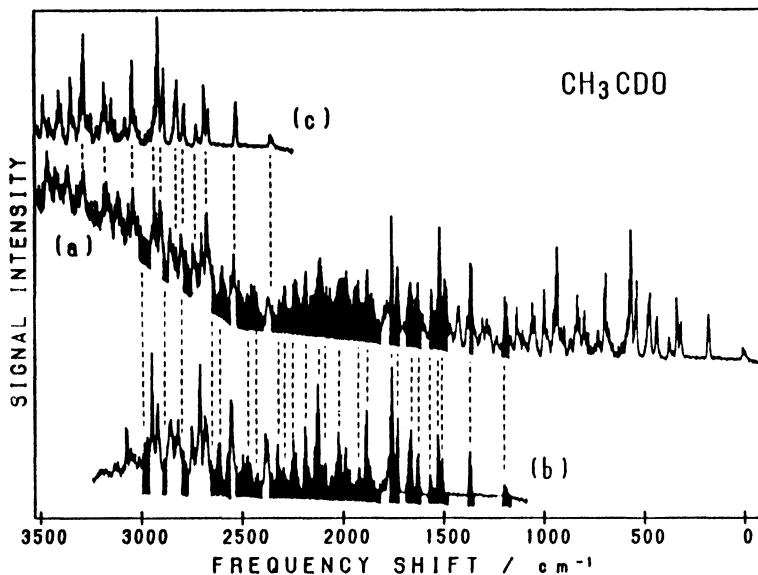


Figure 9 (a) Excitation spectrum of CH_3CDO synthesized from the LIF-excitation and PHOFEX spectra shown in Figure 4. (b) The same spectrum as (a) shifted by ν_4 (1189 cm^{-1}) to the higher energy. (c) The same spectrum as (a) shifted by $2\nu_4$ (2350 cm^{-1}). Shaded bands in (b) belong to 0_0^0 , while those shaded in (a) belongs to 4_0^1 .

$$\tilde{\nu}/n = A + Bn.$$

The anharmonicity B is about 1% of the fundamental frequency for all compounds. The fundamental frequencies of about 1200 cm⁻¹ for the C=O stretching in S₁ may be compared with the corresponding values of 1743 cm⁻¹ for CH₃CHO in the ground electronic state.⁸ A large decrease of frequency is due to the increased antibonding character of the C=O π bonding in the excited state.

The frequency of the C=O stretching depends more strongly on the deuteration of the α hydrogen than that of the methyl group. The frequency shifts on the methyl deuteration (CH₃CHO to CD₃CHO, and CH₃CDO to CD₃CDO) are estimated to be about 1.7% on the basis of the calculation in which CH₃CH or CH₃CD is considered to be a mass point. The observed shifts (0.6 and 0.9%, respectively) are smaller than this estimation. A similar estimation gives the shifts of 0.7 and 0.6%, respectively, for the α deuteration (CH₃CHO to CH₃CDO, and CD₃CHO to CD₃CDO), while the observed shifts (2.3 and 2.6%, respectively) are much higher, suggesting appreciable coupling of the C=O stretching with the HCO bending and/or the CH stretching.

Noble *et al.*^{9,10} and Baba *et al.*¹¹ have previously concluded that most of the bands observed in the lower frequency region (< 0₀⁰ + 1000 cm⁻¹) in the LIF-excitation spectrum of acetaldehyde can be assigned to the fundamental, overtone and combination bands of the ν_{10} , ν_{14} and ν_{15} modes. The methyl torsion (ν_{15}) shows a characteristic feature due to the hindered rotation, which tends to disappear above ~500 cm⁻¹ corresponding to the barrier for the internal rotation. The congested structure appearing in the 500~1200 cm⁻¹ region should be assigned to the combinations of ν_{10} and/or ν_{14} with ν_{15} .

The ν_{14} (the C=O out-of-plane wagging) mode has a double-minimum potential with a barrier of 540 cm⁻¹ for CH₃CHO.¹¹ This is because the molecule deforms out-of-plane in the S₁ state. The vibronic progression due to ν_{14} would, therefore, exhibit a complicated pattern around the barrier top. An additional complication arises in this molecule, since the group-theoretical consideration is not helpful; the vibronic transitions to the states which are symmetric with respect to the molecular plane are symmetry allowed, but have very weak intensity. On the other hand, the antisymmetric vibrational states can be observed due to the vibronic coupling with higher-energy allowed electronic transitions. The intensities arising from both sources are comparable with each other in this case. This situation, together with the existence of lower barriers both for the ν_{14} and ν_{15} modes, have made the previous assignments difficult in the 0~1200 cm⁻¹ region.

In the present study, we have succeeded in obtaining well resolved spectra for four isotope species of acetaldehyde to much higher energy than previously reported and also in separating the vibronic progression starting at 0₀⁰ unequivocally from those starting at 4₀¹ and 4₀². Now we are in the position that we could reexamine the assignment in the 0~1200 cm⁻¹ region thoroughly, since we know which bands belong to the progression starting at 0₀⁰ and we can compare the effects of deuteration at methyl- and α -position completely. The assignment is being performed in our laboratory and will be published in near future.

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