

Laser-induced excitation and dispersed fluorescence spectra of the ethoxy radical

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Abstract. Extensive laser excitation and dispersed fluorescence spectra of the ethoxy (C_2H_5O) radical have been recorded in a supersonic jet expansion. Neon transitions have been used to calibrate both the wavelength of the excitation dye laser and the optical multichannel analyser system used to record the wavelength-resolved emission spectra. Both the excitation and dispersed spectra are characterized by prominent progressions involving the C–O stretch vibrational mode. Seven vibrational frequencies for the excited B^2A' electronic state and eight for the ground X^2A'' state have been assigned. To the best of our knowledge, 10 of these 15 assigned frequencies are reported here for the first time. Vibrational and anharmonic constants for the C–O stretch (ν_{10}) mode have been determined via least-squares fits for the X state ($\omega''_{10} = 1078\text{ cm}^{-1}$, $x''_{10} = 6.2\text{ cm}^{-1}$) and the B state ($\omega'_{10} = 609\text{ cm}^{-1}$, $x'_{10} = 3\text{ cm}^{-1}$).

1. Introduction

The alkoxy radicals, methoxy (CH_3O), ethoxy (C_2H_5O) and isopropoxy ($i-C_3H_7O$), have great theoretical and practical significance. These molecules are reactive intermediates in combustion and oxidation reactions involving hydrocarbons. A large number of investigators [1] have studied the spectroscopy and the electronic structure of the CH_3O radical in detail. The larger molecules, C_2H_5O and $i-C_3H_7O$, have received much less attention [2]. In this paper, we will focus on the C_2H_5O radical. It belongs to the C_s point group and has 18 vibrational frequencies [3]. Four vibrational frequencies have been reported earlier by Inoue *et al* [4] and Ebata *et al* [5], but only one, namely the CO stretch, has been assigned definitively. Miller *et al* [6, 7] have published the rotationally resolved electronic excitation spectra of C_2H_5O for the C–O stretch mode involving the excited vibrational states with $v' = 0, 1$ and 2. Analysis of the emission spectra of C_2H_5O is much more difficult than for CH_3O , because not only is the laser-induced fluorescence (LIF) signal much weaker, but also the dispersed spectra are more congested for the heavier molecule. In the present study, we have employed the supersonic jet expansion technique to record extensive laser excitation spectra (with 0.2 cm^{-1} resolution) and an optical multichannel analyser system to obtain dispersed spectra (with 23 cm^{-1} resolution) of the rovibronically cold ethoxy radical. Seven molecular vibrational frequencies have been determined for the excited B^2A' state and eight frequencies for the ground X^2A'' state. To the best of our knowledge, of the 15 assigned vibrational frequencies, ten (six for the excited B state and four for the ground X state) are reported here for the first time. In addition, vibrational and anharmonic constants

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have been obtained via least-squares fits for the C–O stretch (ν_{10}) mode for both the ground X state and the excited B state.

2. Experimental

The precursor used for generating the C_2H_5O radical was ethyl nitrite (C_2H_5ONO). It was synthesized following a well established protocol [8] using a mixture of $NaNO_2$ and C_2H_5OH and dropwise addition of H_2SO_4 . Freshly synthesized C_2H_5ONO was stored in a steel cylinder at room temperature. Helium was used as a carrier gas and mixed with the ethyl nitrite in the ratio 100:1 by volume. The helium–nitrite mixture (at a typical pressure of 14 atm) was introduced into a vacuum chamber through a pulsed valve (General Valve IOTA ONE) with a 0.5 mm orifice. The typical pressure in the expansion chamber was 1×10^{-4} Torr, with the open duration of the pulsed valve set at 200 μs . Ethyl nitrite seeded in the supersonic jet expansion was photolysed by laser pulses at 248 nm from an excimer laser (Questek ImPulse 4530). The C_2H_5O molecules generated *in situ* were then excited by tunable dye laser (Spectra Physics PDL-3) radiation that was frequency-doubled by employing an autotracker (Inrad Autotracker II). The dye laser itself was pumped by the second harmonic of a Nd:YAG laser (Quanta Ray GCR-11). All of the lasers and the pulse valve ran at 10 Hz. The separation between the photolysis and excitation lasers was typically 10–12 mm, and the delay between the two lasers was $\sim 8 \mu s$. Exciton dyes DCM and LDS 698 were used for the dye laser to cover the spectral region from 610–700 nm. The nominal linewidth of the dye pulse was 0.07 cm^{-1} . LIF from the excited ethoxy radicals was collected by a quartz lens at right angles to both the laser beams and was detected by a photomultiplier tube (Hamamatsu R4220). Excitation spectra were recorded by scanning the dye laser and using a boxcar averager in conjunction with an IBM-compatible AT microcomputer. Wavelength calibration of the spectra was carried out using the optogalvanic transitions excited within a hollow-cathode Fe–Ne lamp [9]. An optical multichannel analyser system (EG & G Princeton Applied Research OMA-4) was employed to record dispersed fluorescence spectra of ethoxy. It included a 0.275 m spectrograph (ARC SpectraPro 275), a lens-coupled intensifier, a 256×1024 element CCD array cooled to $-120^\circ C$ and a data processor. The resolution of the single vibronic level wavelength-resolved emission spectra was $\sim 23 \text{ cm}^{-1}$ in the near UV and visible region. Wavelength calibration was accomplished for each dispersed spectrum using emission lines from an Fe–Ne lamp.

3. Results and discussion

The excitation spectrum of jet-cooled C_2H_5O in the region $29\,100\text{--}32\,200 \text{ cm}^{-1}$ is shown in figure 1. The spectrum is much less congested than that observed in a flow cell at room temperature by Inoue *et al* [4], and hence the band frequencies can be determined accurately. In this paper we discuss the vibronic analysis of the $B \ ^2A' \text{--} X \ ^2A''$ transition; the line positions reported here correspond to the centres of the observed bands. The laser excitation spectrum exhibited one dominant progression with vibrational spacings decreasing from 603 to 580 cm^{-1} , which was assigned to the C–O stretch (ν_{10}) vibrational mode. The first member of the progression at $29\,181 \text{ cm}^{-1}$ was assigned as the 0_0^0 band. As the excitation dye laser has been calibrated precisely with optogalvanic lines of neon, the wavenumbers we have obtained are expected to be more reliable than those reported by Inoue *et al* [4]. There are six other progressions with relatively smaller amplitudes

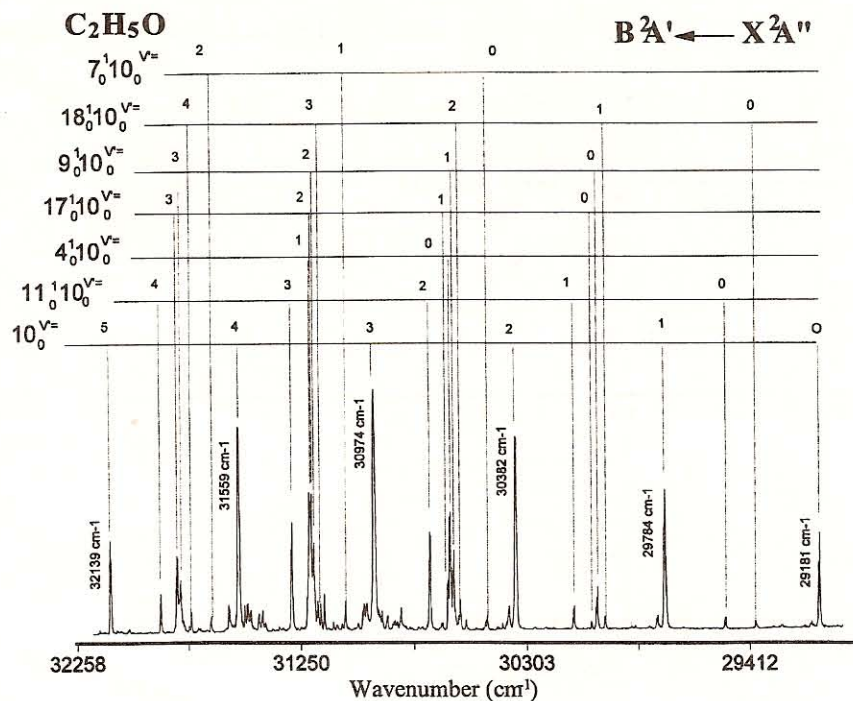


Figure 1. Laser excitation fluorescence spectrum of the $B^2A' \leftarrow X^2A''$ system of the C_2H_5O radical. The time delay between the excimer laser and the dye laser was $8 \mu s$.

starting at 29 425, 29 543, 30 050, 30 074, 30 504 and 30 641 cm^{-1} , respectively, which also have associated C–O stretch vibrational intervals. We have identified and assigned these features as bands that are in combination with the C–O stretch (ν_{10}) mode. The vibrational frequencies for similar symmetric top molecules, namely C_2H_5F , C_2H_5Cl and C_2H_5Br , were used as a reference [10] for the assignment of the C_2H_5O vibrations, because all of these C_2H_5X molecules possess C_s symmetry. We have assigned seven vibrational frequencies for the excited B^2A' state, namely $\nu'_4 = 1460 \text{ cm}^{-1}$ (CH_2 scissors), $\nu'_7 = 1323 \text{ cm}^{-1}$ (CH_2 wag), $\nu'_9 = 869 \text{ cm}^{-1}$ (CC stretch), $\nu'_{10} = 603 \text{ cm}^{-1}$ (CO stretch), $\nu'_{11} = 362 \text{ cm}^{-1}$ (CCO deformation), $\nu'_{17} = 893 \text{ cm}^{-1}$ (CH_2 rocking) and $\nu'_{18} = 244 \text{ cm}^{-1}$ (torsion). Except for the CO stretch (ν'_{10}), to the best of our knowledge the remaining six excited-state vibrational frequencies are reported here for the first time. We have investigated the structure of the individual bands in the excitation spectra. All of the vibrational modes recorded in excitation showed similar structure, except the bands involving the ν_{17} and ν_{18} modes, and also bands that were in combination with either ν_{17} or ν_{18} . As per symmetry classification of symmetric tops of C_s symmetry [10], the 18 vibrational modes of C_2H_5O can be divided into two groups. The modes ν_1 to ν_{11} belong to the symmetry species a' , whereas the modes ν_{12} to ν_{18} belong to species a'' . The bands belonging to the two different symmetry species (a' or a'') were found to have different spectral appearance and structure. Figure 2 shows a comparison of three LIF excitation scans for bands 10_0^1 , 17_0^1 and $10_0^1 18_0^1$. One can clearly see that there are two distinct patterns. The 10_0^1 band has one kind of structure, while the other two bands (17_0^1 and $10_0^1 18_0^1$) are alike but have distinctively different structures compared with the 10_0^1 band. It is for this reason that we assigned the vibrational feature at 893 cm^{-1} (in figure 1) as ν'_{17} (rather than ν'_9). We also observe

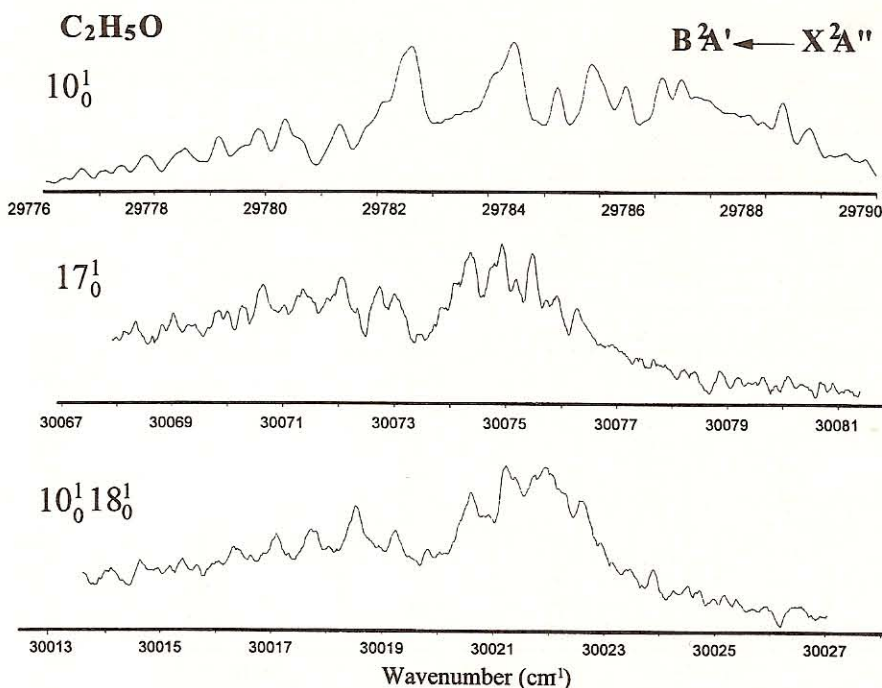


Figure 2. Patterns observed in the laser-excited spectra of C_2H_5O for B-X 10_0^1 , 17_0^1 and $10_0^1 18_0^1$ bands. The bands 17_0^1 and $10_0^1 18_0^1$ have the same pattern, while band 10_0^1 has a distinctly different structure.

that the spectrum involving the ν_{17} mode exhibits better resolution than that involving ν_{18} , although both spectra were taken under identical conditions. A possible explanation for such an observation is that there are more rotational transitions occurring in the ν_{18} band, which our recording system was unable to resolve. The observed frequencies of the vibrational bands obtained in excitation and the corresponding assignments are listed in table 1. There are two other bands located towards the higher wavenumber side of the 10_0^0 band, which are *only* 29 and 55 cm^{-1} from the 10_0^0 band, and these have progressions built upon them with the same CO stretch spacing interval. We have labelled these two bands as a_0^1 and b_0^1 in table 1, because these are *unidentified* low-frequency vibrations for the ethoxy molecule.

Dispersed fluorescence spectra have also been obtained for the C_2H_5O radical and these exhibit better resolution than the spectra reported by Inoue *et al* [4] and Ebata *et al* [5], which is due to the isolated supersonic jet environment that we have employed for generation of the radical. Here we report the observed vibrational intervals excited when the bands 10_0^0 , 10_0^1 , 10_0^2 , 10_0^3 and 10_0^4 are pumped and dispersed. All of the recorded intervals for the above-cited bands, together with the corresponding averages and vibrational assignments, have been collected in table 2. Additional CO-stretch ($\sim 1060\text{ cm}^{-1}$) progressions starting at 335.68 nm (29790 cm^{-1}), 329.34 nm (30364 cm^{-1}) and 323.26 nm (30935 cm^{-1}), respectively, have been assigned to *vibrationally relaxed* bands from the $v' = 1, 2, 3$ levels of the excited state when the 10_0^2 , 10_0^3 and 10_0^4 bands were pumped. All of these relaxation transitions have been collectively assigned as $10^{v'-1}$ in table 2. Figures 3 and 4 are illustrations of the dispersed spectra obtained when the 10_0^0 and 10_0^3 bands, respectively, were excited. Wavelength-resolved emission spectra for these two bands of C_2H_5O are

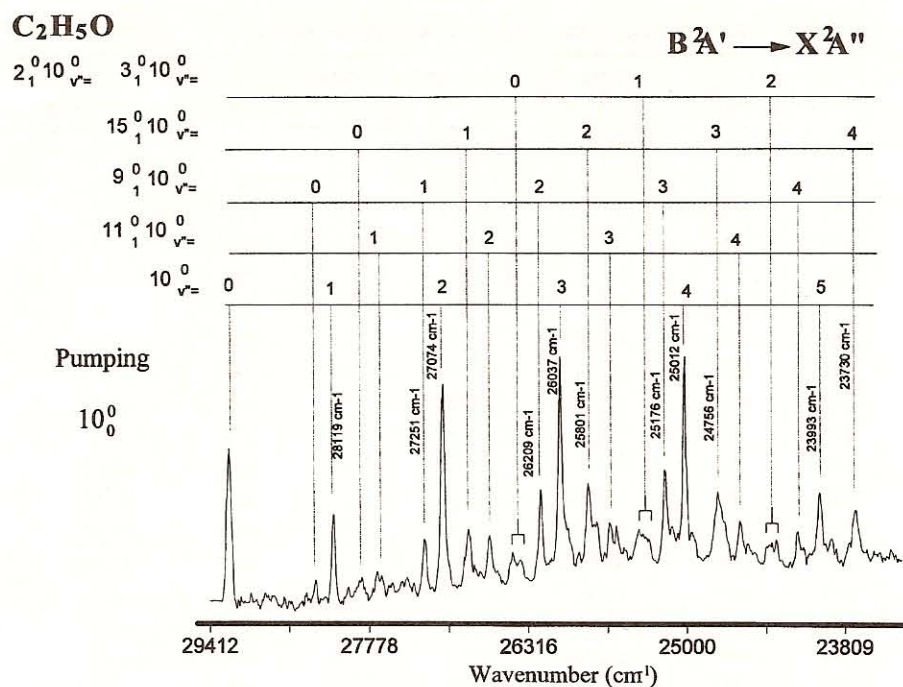


Figure 3. The dispersed spectrum of the B-X 10_0^0 band of C₂H₅O. The frequency of the pump laser was 29 179 cm⁻¹ and the time delay between the excimer and dye lasers was 5 μs.

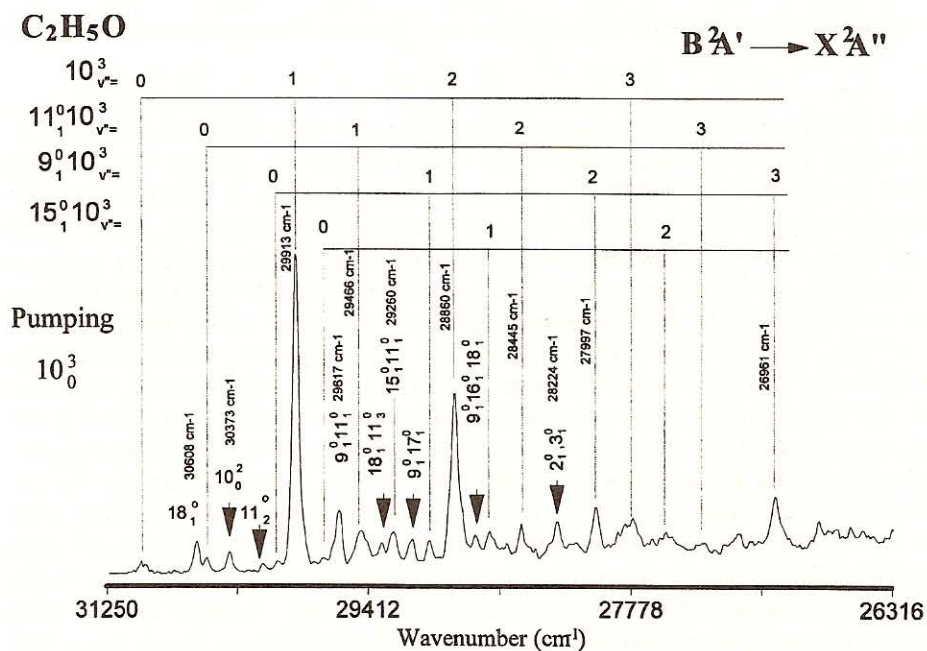


Figure 4. The dispersed spectrum of the B-X 10_0^3 band of C₂H₅O. The frequency of the pump laser was 30 972 cm⁻¹ and the time delay between the excimer and dye lasers was 5 μs.

Table 1. Observed bands in the C₂H₅O B ← X excitation spectrum.

Wavenumber (cm ⁻¹)	Relative intensity	Rel. to 10 ₀ ⁰ (cm ⁻¹)	Vibrational assignment	Wavenumber (cm ⁻¹)	Relative intensity	Rel. to 10 ₀ ⁰ (cm ⁻¹)	Vibrational assignment
29 181	272	0	10 ₀ ⁰	31 005	78	1824	a ₀ ¹ 10 ₀ ³
29 210	35	29	a ₀ ¹	31 017	77	1836	b ₀ ¹ 10 ₀ ³
29 236	23	55	b ₀ ¹	31 096	52	1915	7 ₀ ¹ 10 ₀ ¹
29 425	38	244	18 ₀ ¹	31 109	30	1928	
29 543	47	362	11 ₀ ¹	31 133	19	1952	
29 784	321	603	10 ₀ ¹	31 147	23	1966	
29 812	40	629	a ₀ ¹ 10 ₀ ¹	31 170	15	1989	
29 845	22	664	b ₀ ¹ 10 ₀ ¹	31 187	107	2006	
30 022	50	841	18 ₀ ¹ 10 ₀ ¹	31 202	82	2021	18 ₀ ¹ 10 ₀ ³
30 050	129	869	17 ₀ ¹	31 213	68	2032	
30 074	35	893	9 ₀ ¹	31 230	230	2049	4 ₀ ¹ 10 ₀ ¹
30 146	62	965	11 ₀ ¹ 10 ₀ ¹	31 249	381	2068	9 ₀ ¹ 10 ₀ ²
30 382	524	1201	10 ₀ ²	31 241	349	2060	17 ₀ ¹ 10 ₀ ²
30 410	75	1229	a ₀ ¹ 10 ₀ ²	31 326	226	2145	11 ₀ ¹ 10 ₀ ³
30 437	30	1256	b ₀ ¹ 10 ₀ ²	31 559	555	2378	10 ₀ ⁴
30 504	50	1323	7 ₀ ¹	31 599	80	2418	a ₀ ¹ 10 ₀ ⁴
30 614	94	1433	18 ₀ ¹ 10 ₀ ²	31 679	34	2498	a ₀ ¹ 10 ₀ ⁴
30 641	197	1460	4 ₀ ¹	31 770	59	2589	18 ₀ ¹ 10 ₀ ⁴
30 653	327	1472	17 ₀ ¹ 10 ₀ ¹	31 819	135	2638	
30 665	142	1484	9 ₀ ¹ 10 ₀ ¹	31 833	210	2652	9 ₀ ¹ 10 ₀ ³
30 740	200	1559	11 ₀ ¹ 10 ₀ ²	31 907	84	2726	11 ₀ ¹ 10 ₀ ⁴
30 974	628	1793	10 ₀ ³	32 139	218	2958	10 ₀ ⁵

reported in this paper for the *first time*. In the spectrum for the 10₀⁰ band (see figure 3), one can clearly identify the main progression with a vibrational spacing that decreases from 1070 to 1019 cm⁻¹ to be the CO stretch mode (ν''_{10}) in the X ²E state. The CO stretch is the most active vibrational mode. Progressions with intervals corresponding to ν''_{10} are built on other distinct frequencies, and these have been assigned as bands in combination with ν_{10} . Fundamental vibrational frequencies of C₂H₅F, C₂H₅Cl and C₂H₅Br, have been used as a reference [10] for assignment of the distinct ethoxy frequencies for the CC stretch ($\nu''_9 = 910$ cm⁻¹), CCO deformation ($\nu''_{11} = 444$ cm⁻¹) and the CH₂ twist ($\nu''_{15} = 1277$ cm⁻¹). The 444 cm⁻¹ feature could not be seen when the 10₀⁰ band was pumped (see figure 3), although it was quite obvious when the other bands, such as 10₀³ (see figure 4), were pumped. There are three other wide peaks located at average wavenumber intervals (as indicated in table 2) of 2753, 3818 and 4834 cm⁻¹, respectively. Our OMA-based system was unable to resolve the finer details of these peaks and it appears that these are blended ν_2 (CH₂ s-stretch) and ν_3 (CH₃ s-stretch) features. A transition located at an average value of 370 cm⁻¹ to the red of the pump line can be seen clearly when bands 10₀¹, 10₀², 10₀³ and 10₀⁴ were dispersed (for example, this feature is visible in figure 4 when band 10₀³ was wavelength-resolved) and was assigned as low-frequency torsion (ν''_{18}). The observed vibrational frequencies of ethoxy, along with those of C₂H₅F, C₂H₅Cl, C₂H₅Br, are listed in table 3. Four of the identified vibrational frequencies, ν''_7 , ν''_9 , ν''_{10} and ν''_{11} agree with Inoue *et al*'s assigned frequencies [4] to within the resolution of our detector

Table 2. Observed vibrational transitions in the $C_2H_5O B \rightarrow X$ dispersed spectra. The wavenumbers listed are the differences between the pump frequency and the corresponding emission frequencies (in cm^{-1}).

10^0_0 (cm^{-1})	Relative intensity	Pumped band								Average intensity (cm^{-1})	Assignment
		10^1_0 (cm^{-1})	Relative intensity	10^2_0 (cm^{-1})	Relative intensity	10^3_0 (cm^{-1})	Relative intensity	10^4_0 (cm^{-1})	Relative intensity		
		361	443	366	7242	386	8716	367	2540	370	ν_{18}
				438	5842	450	4263	445	2377	444	ν_{11}
				592	7837	610	5785	624	3349	609	$10\nu'^{-1}$
								812	2279	812	$\nu_{11} + \nu_{18}$
		850	1702			853	2523			852	$2\nu_{11}$
899	3075					943	3371	920	1896	910	ν_9
								984	2237	984	ν_{17}
		984	114							984	ν_{16}
1070	16153	1065	30825	1059	67871	1073	87410	1071	18919	1068	ν_{10}
1225	1530									1225	$2\nu_{11} + \nu_{18}$
1305	1594			1262	5766			1263	2359	1277	ν_{15}
1349	3665	1361	6484	1349	19162	1366	17120	1379	3648	1361	$\nu_9 + \nu_{11}$
1498	4816	1500	7263	1494	14655	1511	11505	1495	3582	1500	$\nu_{11} + \nu_{10}$
1640	2436	1638	3136	1638	12131	1646	8300	1645	2118	1641	$3\nu_{11} + \nu_{18}$
1733	2770	1729	9868	1715	12982	1720	11320	1713	3191	1722	$\nu_{15} + \nu_{11}$
1845	2518	1838	4740	1828	9241	1850	9274	1842	4142	1841	$\nu_9 + \nu_{17}$
1950	10881	1945	5501	1950	7801	1959	9065	1959	8587	1953	$\nu_9 + \nu_{10}$
2122	42671	2118	50665	2117	83601	2118	49267	2130	7972	2121	$2\nu_{10}$
		2245	3682	2255	14969	2251	10485	2259	3632	2252	$\nu_9 + \nu_{16} + \nu_{18}$
2357	13253	2354	14122	2337	20013	2336	11320	2338	2955	2344	$\nu_{15} + \nu_{10}$
2456	4819	2444	6526	2446	11056	2446	11522	2446	3168	2448	$\nu_9 + \nu_5$
2543	11972	2535	12317	2535	20800	2539	13656	2534	3361	2537	$\nu_{11} + 2\nu_{10}$
2778	8653	2759	10289	2748	18714	2753	14168	2760	3708	2753	ν_2 & ν_3
2991	21271	2983	5229	2983	9004	2987	18018	3000	7929	2989	$\nu_9 + 2\nu_{10}$
3053	7052	3048	7225	3068	11528	3067	8022			3059	$\nu_{17} + 2\nu_{10}$
3160	48199	3158	32374	3155	36083	3168	13835	3152	1297	3158	$3\nu_{10}$
3231	13564			3311	18786	3322	9619	3328	3106	3320	$\nu_{15} + \nu_{16} + \nu_{10}$
3397	22522	3401	16656	3394	16903	3401	11435	3374	2614	3393	$\nu_{15} + 2\nu_{10}$
3464	14840	3464	11118	3474	12546					3467	$\nu_{18} + 3\nu_{10}$
3577	14653							3600	2502	3688	$\nu_{11} + 3\nu_{10}$
3632	14067	3621	9944	3614	12468	3618	8567	3627	2951	3622	$\nu_9 + \nu_2$
											& $\nu_9 + \nu_3$
3812	13326	3812	13136	3817	15554	3820	11027	3831	3478	3818	$\nu_{10} + \nu_2$
											& $\nu_{10} + \nu_3$
4023	25237			4023	15219	4022	21113	4037	4981	4026	$\nu_9 + 3\nu_{10}$
4187	48192	4183	16939	4181	17670					4184	$4\nu_{10}$
				4350	25600					4350	$\nu_{15} + \nu_{16} + 2\nu_{10}$
4442	20868	4422	13205							4432	$\nu_{15} + 3\nu_{10}$
4610	14952									4610	$\nu_{11} + 4\nu_{10}$
4831	10215			4836	19216					4834	$2\nu_{10} + \nu_2$
											& $2\nu_{10} + \nu_3$
5045	12843									5045	$\nu_9 + 4\nu_{10}$
5206	20672									5206	$5\nu_{10}$
5461	17216									5461	$\nu_{15} + 4\nu_{10}$

system. The remainder of the vibrational frequencies listed in table 3 are reported here for the *first time*. In figure 3 we see clearly four transitions located at 1349, 2357, 3397 and 4442 cm^{-1} , respectively, to the red of the pump frequency. These lines form a progression

with vibrational spacings in the interval 1008–1045 cm^{-1} . Inoue *et al* [4] also reported these four transitions and assigned these as ν_7'' , $\nu_7'' + \nu_{10}''$, $\nu_7'' + 2\nu_{10}''$ and $\nu_7'' + 3\nu_{10}''$, making the argument that the first interval was 1008 cm^{-1} , that is, 60 cm^{-1} less than the frequency $\nu_{10}'' = 1068 \text{ cm}^{-1}$. We doubt the correctness of the above-cited assignments due to Inoue *et al* [4], because there appears to be no reason to cause a combined mode shift towards the pump light by a relatively large vibrational interval of 60 cm^{-1} . Our comprehensive data set and analyses have enabled us to assign the 1349 cm^{-1} transition as $\nu_9'' + \nu_{11}''$. We have assigned the frequency 1277 cm^{-1} to the CH_2 twist mode (ν_{15}'').

Table 3. Vibrational intervals (in cm^{-1}) for several $\text{C}_2\text{H}_5\text{X}$ molecules.

Mode no ^a	Type of mode				B $\text{C}_2\text{H}_5\text{O}$		X $\text{C}_2\text{H}_5\text{O}$	
		$\text{C}_2\text{H}_5\text{Br}$	$\text{C}_2\text{H}_5\text{Cl}$	$\text{C}_2\text{H}_5\text{F}$	Inoue <i>et al</i> ^b	This work	Inoue <i>et al</i> ^c	This work
ν_1	CH_3 d-stretch	2988	2946	3003				
ν_2	CH_2 s-stretch	2937	2967	2941				2753
ν_3	CH_3 s-stretch	2880	2881	2915				2753
ν_4	CH_2 scissors	1451	1448	1479		1460		
ν_5	CH_3 d-deform	1451	1463	1449				
ν_6	CH_3 s-deform	1386	1385	1395				
ν_7	CH_2 wag	1252	1289	1365		1323	1367	
ν_8	CH_3 rock	1061	1081	1108				
ν_9	CC stretch	964	974	1048		869	873	910
ν_{10}	CX stretch	583	677	880	596	603	1060	1068
ν_{11}	CCX deform	290	336	415		362	422	444
ν_{12}	CH_2 deform	3018	3014	3003				
ν_{13}	CH_3 d-stretch	2988	2986	3003				
ν_{14}	CH_3 d-deform	1451	1448	1449				
ν_{15}	CH_2 twist	1248	1251	1277				1277
ν_{16}	CH_3 rock	964	974	1048				984
ν_{17}	CH_2 rock	770	786	810		893		943
ν_{18}	Torsion	247	251	243		244		370

^a Reference [10].

^b Reference [4], table I.

^c Reference [4], table II.

The vibrational and anharmonic constants for the C–O stretch mode (ν_{10}) have been determined by a least-squares fit of the members of a progression to the following equation [11]:

$$\nu - \nu_0 = (0.5\omega'_{10} - 0.5\omega''_{10} - 0.25x'_{10} + 0.25x''_{10}) - \omega'_{10}(v'_{10} + 0.5) + \omega''_{10}(v''_{10} + 0.5) + x'_{10}(v'_{10} + 0.5)^2 - x''_{10}(v''_{10} + 0.5)^2$$

where a single prime indicates the upper state and a double prime denotes the lower state. Here ν_0 is the band origin, ω_{10} is the vibrational constant, x_{10} is the anharmonic parameter and v_{10} is the vibrational quantum number for the ν_{10} mode. We have obtained: $\omega'_{10} = 609 \text{ cm}^{-1}$, $\omega''_{10} = 1078 \text{ cm}^{-1}$, $x'_{10} = 3.0 \text{ cm}^{-1}$ and $x''_{10} = 6.2 \text{ cm}^{-1}$. The standard deviations of the fit were 0.3 and 2.3 cm^{-1} for the excited state and the ground state, respectively.

Acknowledgments

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