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Hole Burning Spectrum of the Vinoxy Radical in the $\tilde{B}(^2A'')$ State in a Supersonic Free Jet

Tatsuo GEJO,† Masao TAKAYANAGI,†,†† Takumi KONO,† and Ichiro HANAZAKI†,††,*
†The Graduate University for Advanced Studies, Myodaiji, Okazaki 444
††Institute for Molecular Science, Myodaiji, Okazaki 444

The vibronic structure of the vinoxy radical in the $\tilde{B}(^2A'')$ state was investigated by the hole burning technique in a supersonic free jet. Frequencies of the vibronic bands were determined accurately up to 4000 cm^{-1}. It is shown that most of them can be assigned to the combinations of v_4-v_9 vibrational modes, in agreement with the previous calculation.

Several spectroscopic studies have been reported[1-5] on the vinoxy radical (CH_2CHO), since it was postulated to be an important reaction intermediate in combustion.[6] Inoue and Akimoto first observed the fluorescence spectra of the vinoxy radical in the $\tilde{B}(^2A'')$ state, and assigned the observed bands in terms of three skeletal vibrations, i.e., CC and CO stretching and CCO bending.[1] Heaven et al. observed the LIF excitation and dispersed fluorescence spectra in a supersonic jet, from which rotational constants were determined for the ground and excited states.[4] Hunziker et al. reported a study of the kinetic absorption spectroscopy on the $\tilde{B}(^2A'')$ state.[3] Although the absorption spectrum of the vinoxy radical consists of a series of vibronic progressions appearing between 350 nm and 280 nm, only four main bands near the 0-0 band have been observed in the LIF excitation spectrum. This is presumably due to the predissociation of the radical in the excited state.

Recently, Yamaguchi et al. reported a vibrational analysis and a calculation of the Franck-Condon factors for the vibronic transition between the $\tilde{B}(^2A'')$ and $\tilde{X}(^2A'')$ states of the vinoxy radical.[7] They made the normal mode analysis based on an *ab initio* MO calculations and reassigned the bands obtained by Inoue et al., Heaven et al. and Hunziker et al.

In this letter, the vibronic structure of the vinoxy radical in the $\tilde{B}(^2A'')$ state was investigated by measuring the hole burning spectrum[8-9] in a supersonic free jet. In this technique, the frequency of the probe laser is fixed in resonance with one of the vibronic transitions and the resultant total fluorescence is monitored. The pump laser pulse is applied before the probe pulse, and its frequency is scanned. The fluorescence depletion is observed when the pump frequency is in resonance with the transition that has a common initial state with the transition being probed. This technique allows us to observe the bands which can not be observed in the LIF excitation spectra because of a rapid relaxation.

The vinoxy radical was generated by the 193 nm photolysis of EVE (ethyl vinyl ether). Helium containing 10% EVE was expanded into a vacuum chamber from a conventional pulsed valve with a 0.8-mm-diameter orifice. The stagnation pressure of the gas mixture was 2 atm. A pulsed valve with a duration of 1 ms was operated at 10 Hz. EVE (Tokyo Kasei Kogyo Co. 99.0%) was used without further purification. The output of an ArF excimer laser (Lumonics: E-500, 10-mJ/pulse) was focused onto the point 5 mm downstream from the nozzle exit (X/D=6.3) in order to dissociate EVE. The LIF excitation spectra were measured using frequency-doubled output of a pulsed dye laser (Quantel:TDL-50, pulse width:7 ns, spectral width: 0.2-0.3 cm^{-1}) pumped by the frequency-doubled output of a Nd:YAG laser (Quantel: YG5177C). This laser was focused on to the point 16 mm down stream from the nozzle exit (X/D=20). The total fluorescence emitted from the vinoxy radical was collected and focused onto a photomultiplier (Hamamatsu R955) through bandpass filters. The output signal of the photomultiplier was preamplified and integrated by a boxcar averaging system. Intensity of the laser was monitored by a PIN photodiode to correct for the laser power fluctuation. The laser frequency was calibrated simultaneously by recording the optogalvanic spectrum of the Ne atom. The hole burning measurement requires two laser sources; one for pumping and the other for probing. The Nd:YAG-pumped dye laser system mentioned above was used for pumping. Another frequency-doubled output of a pulsed dye laser (Lambda Physik:FL-3002, pulse width: 10 ns, spectral width: 0.1-0.2 cm^{-1}) pumped by an excimer laser (Lumonics: HE-420-SM-B) was used for probing. The delay between the pump and probe lasers was set at 200 ns to prevent the pump laser scattering. The total fluorescence due to the probe laser was collected and processed similarly to the LIF measurement. Intensity of the pump laser was monitored by a PIN photodiode and the pump laser frequency was calibrated by the optogalvanic spectrum.

Figure 1(a) shows an LIF spectrum of the $\tilde{B}(^2A'')\leftarrow\tilde{X}(^2A'')$ transition of the vinoxy radical. The lowest band is the origin band. Its absolute frequency is 28787 cm^{-1}, which may be compared with the literature value 28784 cm^{-1}.4) Additional three intense bands were interpreted as CCO bending (448 cm^{-1}), CC stretching (917

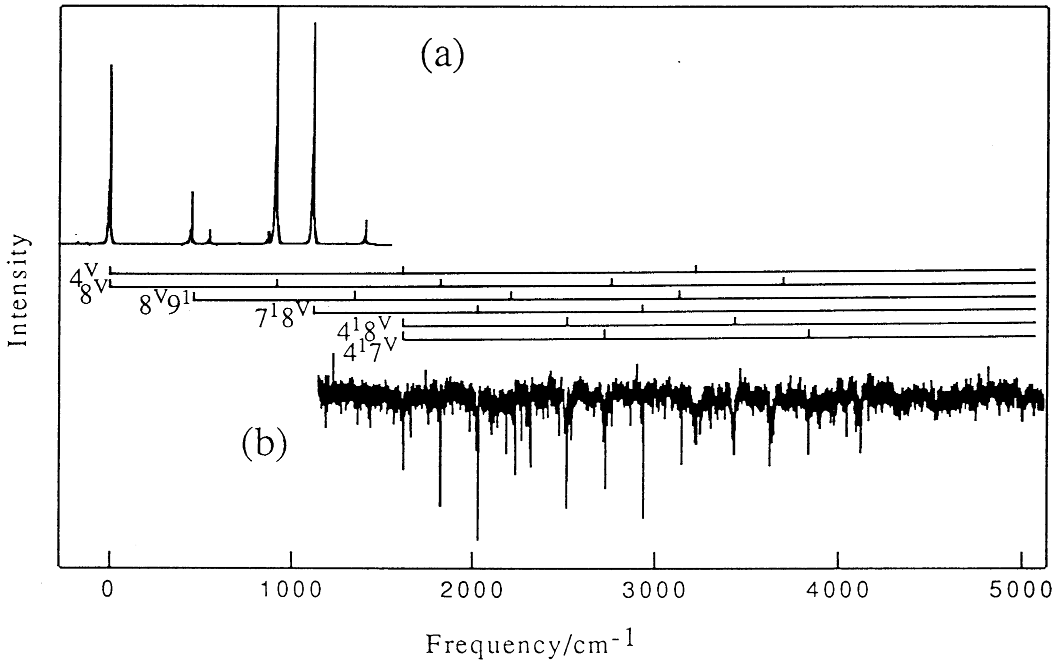

Fig. 1. (a) LIF spectrum of the vinoxy radical for the $\tilde{B}(^2A'')\leftarrow\tilde{X}(^2A'')$ transition. The origin band locates at 28787cm^{-1}. (b) The hole burning spectrum of the vinoxy radical. The ordinate shows the fluorescence intensity.

cm^{-1}) and CH$_2$ rocking (1122 cm^{-1}) by Yamaguchi et al.7) No vibronic band is observable in the region above 1500 cm^{-1} (~330 nm) presumably due to the predissociation. Additional three weak bands were ignored in the previous papers. We assigned that the 872 cm^{-1} band to the CCO-bending overtone (448 cm^{-1}x2) and the 1406 cm^{-1} band to the OCH bending fundamental, which corresponds to the literature value of 1390 cm^{-1}.7) The 546 cm^{-1} band is unassigned but, in view of its low frequency, should be one of ν_{10}, ν_{11} and ν_{12} (Table 1), the frequencies of which have been calculated to be 711 cm^{-1}, 776 cm^{-1} and 379 cm^{-1}, respectively.7)

Table 1. The vibrational modes in the vinoxy radical and fundamental frequencies in the $\tilde{B}(^2A'')$ state. Values in parentheses are from Ref. 4

Mode and character	Symmetry	Frequency /cm^{-1}
ν_1(CH$_2$ asym.str.)	a'	-
ν_2(CH$_2$ sym.str.)	a'	-
ν_3(CH asym.str.)	a'	-
ν_4(CO str.)	a'	1619
ν_5(CH$_2$ sci.)	a'	1433
ν_6(OCH bend.)	a'	1406
ν_7(CH$_2$ rock.)	a'	1122(1122)
ν_8(CC str.)	a'	917(917)
ν_9(CCO bend.)	a'	448(450)
ν_{10}(CH wag.)	a''	-
ν_{11}(CC torsion.)	a''	-
ν_{12}(CH$_2$ wag.)	a''	-

Figure 1(b) shows the hole burning spectrum of the vinoxy radical between 295 and 330 nm which is obtained by fixing the probe laser at 336.7 nm, where the LIF intensity is maximum. The ordinate shows the total fluorescence intensity with depletions when the pump laser is in resonance. Maximum depletion is about 40%. Every band appears in a doublet with a spacing of ~10 cm^{-1}, which corresponds to the P and R branches.5)

Table 2 summarizes the bands observed in the hole burning spectrum of the vinoxy radical together with our assignments based on the fundamental frequencies given in Table 1. It is seen that most of the bands can be assigned in terms of ν_4-ν_9. Among the normal modes listed in Table 1, ν_1, ν_2 and ν_3 are expected to be weak since they are of the CH stretch character, which should be less affected by the π-π* type electronic transition. The ν_{10}, ν_{11} and ν_{12} modes should also be weak since they are of a'' symmetry. The discrepancy between the

Table 2. Assignments of the vibronic bands observed in the hole burning spectrum for the $\tilde{B}(^2A'') \leftarrow \tilde{X}(^2A'')$ transition of the vinoxy radical

Frequency /cm^{-1}	Assignments a)	Relative depth b)	Calculated intensity c)	Frequency/ cm^{-1}	Assignments	Relative depth b)	Calculated intensity c)
1363	$8^1 9^1$(1365)		18	2478	$7^1 8^1 9^1$(2487)		-
1433	5^1(1433)		17	2519	$4^1 8^1$(2536)	74	97
1565	$7^1 9^1$(1570)		-	2543	$5^1 7^1$(2555)		-
1619	4^1(1619)	57	100	2732	$4^1 7^1$(2741)	71	43
1659	$7^1 X^1$(1668)		-	2767	8^3(2751)		-
1757	$8^1 9^2$(1813)		-	2939	$7^1 8^2$(2956)	74	16
1823	8^2(1834)	76	40	3147	$8^3 9^1$(3199)		-
2033	$7^1 8^1$(2039)	100	37	3226	4^2(3238)		68
2188	$4^1 X^1$(2165)		-	3433	$4^1 8^2$(3453)		43
2235	7^2(2244)		-	3627	$4^1 7^1 8^1$(3658)		39
2269	$8^2 9^1$(2282)		-	3836	$4^1 7^2$(3863)		29
2322	$6^1 8^1$(2323)		25	4121	$4^2 8^1$(4155)		64

a) X is an unassigned band with a'' symmetry appearing at 546 cm^{-1} (see text). Values in parentheses are calculated from the fundamental frequencies in Table 1. b) Relative depths are normalized to the most intense peak at 2033 cm^{-1}. c) Relative values of the Franck-Condon factor calculated in Ref. 7.

observed frequency and the simple sums of the fundamental frequencies are well accounted for by the anharmonicity, except for the 4^1X^1 and 8^3 bands for which the Fermi resonance may cause additional shifts of frequency. This results confirm the previous assignments7) almost completely. However, the frequencies of the bands given in Table II have been determined by the hole burning technique much more accurately than the previous values determined on the basis of broad bands in the absorption spectrum.7)

Relative depths of the hole burning spectrum seem to be inconsistent with the calculated Franck-Condon factors7) (Table 2). To confirm that the difference is not caused by the saturation of transitions in our experiment, we measured the relative depth for five combination bands (8^2, 7^18^1, 4^18^1, 4^17^1 and 8^27^1) and a fundamental band (4^1) at the same pump laser power which is well below the saturation level (Table 2). Our result shows that the overtone and combination bands including the ν_8 mode have larger depths than the ν_4 fundamental band, while the calculated Franck-Condon factor is largest for 4^1.7) The single-vibronic-level fluorescence spectrum shows also that the CO stretching (ν_4) is predominant.2,7) The discrepancy may be caused by the Dushinsky effect7,10,11) which is possibly more pronounced than that predicted theoretically.

Two reaction channels may be responsible for the depletion of the vinoxy radical in the $\tilde{B}(^2A'')$ state:

$$CH_2CHO \rightarrow CH_2 + HCO \quad (1)$$

$$CH_2CHO \rightarrow CH_3 + CO \quad (2).$$

Jacox indicated reaction (2) to be an important reaction on the basis of the argon matrix experiment.4) We tried to detect HCO, one of the products of (1), with the LIF technique using a third dye laser to excite the $\tilde{B} \leftarrow \tilde{X}$ transition of HCO.12) The pump laser was fixed at 319.5 nm (2033 cm^{-1}) where depletion of the hole burning was largest. No additional HCO was observed to that produced directly in the photodissociation of EVE. It is therefore most probable that channel (2) is dominant in the decay of the $\tilde{B}(^2A'')$ state of the vinoxy radical.

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