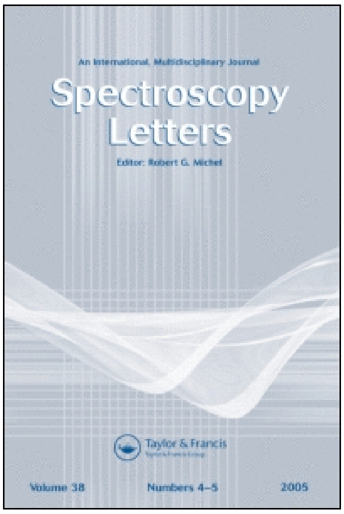

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Prabhakar Misra[a]; Xinming Zhu[a]
[a] Laser Spectroscopy Laboratory, Department of Physics and Astronomy, Howard University, Washington, D.C.

To cite this Article Misra, Prabhakar and Zhu, Xinming(1993) 'Laser Excitation Spectroscopy of the Jet-Cooled Methoxy Radical Amidst Hydroxyl Transitions', Spectroscopy Letters, 26: 2, 389 — 402
To link to this Article: DOI: 10.1080/00387019308011539
URL: http://dx.doi.org/10.1080/00387019308011539

SPECTROSCOPY LETTERS, 26(2), 389-402 (1993)

LASER EXCITATION SPECTROSCOPY OF THE JET-COOLED METHOXY RADICAL AMIDST HYDROXYL TRANSITIONS

Key Words: Laser-Induced Fluorescence, UV Spectroscopy, Methoxy Radical, Supersonic Jet Expansion.

Prabhakar Misra* **and Xinming Zhu**

Laser Spectroscopy Laboratory
Department of Physics and Astronomy
Howard University, Washington, D.C. 20059

ABSTRACT

Laser-induced fluorescence excitation spectra of the methoxy radical have been recorded under high resolution in a supersonic jet expansion. The rotational structure associated with the 3^1_0 band of methoxy has been identified in the midst of strong overlapping rotational transitions due to the hydroxyl radical in the 32240 - 32580 cm^{-1} spectral region. Rotationally-resolved $\tilde{A}\ ^2A_1$ - $\tilde{X}\ ^2E$ spectra of the 3^1_0 band of methoxy have been explicitly assigned using the nomenclature for prolate symmetric top transitions in doublet states.

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*Author to whom correspondence should be addressed.

Introduction

The methoxy (CH_3O) radical is an important chemical intermediate in air pollution and in combustion processes.[1] Laser Induced Fluorescence (LIF) spectroscopy in the near ultraviolet[2] can help detect CH_3O and yield information about the excited electronic state involved in the $\tilde{A}\ ^2A_1 - \tilde{X}\ ^2E$ transition via recording of excitation spectra of sufficient resolution. The LIF spectroscopy of methoxy serves a dual purpose: it can be a sensitive diagnostic tool in studying the progress of important atmospheric and combustion reactions in which CH_3O participates as a free radical intermediate and at the same time provide crucial information about the structure of the electronic states involved in the CH_3O transitions.

In the current investigation, we have used a supersonic jet expansion in conjunction with a tunable dye laser to study the 32240 - 32580 cm^{-1} spectral region, where both the methoxy (CH_3O) and hydroxyl (OH) radicals yield laser-induced fluorescence. Rotationally-resolved $\tilde{A} - \tilde{X}$ transitions for the 3^1_0 band of CH_3O have been obtained around 32305 cm^{-1} and assigned in the midst of strong overlapping OH rotational transitions arising from the $A\ ^2\Sigma^+ - X\ ^2\Pi_i$ (0,0) band system. The methoxy transitions were assigned following the previous work of Misra done in association with Miller and coworkers.[3,4] The interfering OH transitions in the spectral region under investigation were identified explicitly following the earlier work of Dieke and Crosswhite.[5] We have identified nitrous acid (HONO) as the precursor for the generation of OH radicals. HONO is present as an impurity during the synthesis of methyl nitrite (CH_3ONO). As a consequence, both OH and CH_3O radicals are formed in the free jet expansion following photodissociation of the precursor by an excimer laser.

The tunable dye laser used to probe the excited state energy levels had a narrow line-width of 0.05 cm^{-1} and enabled us to record high resolution excitation spectra of methoxy. Rotationally-resolved $\tilde{A}\ ^2A_1 - \tilde{X}\ ^2E$ spectra of the 3^1_0 band of CH_3O have been explicitly assigned employing the nomenclature for prolate symmetric top transitions in spin doublet states.

Experimental

Methyl nitrite (CH_3ONO) was the precursor for the CH_3O radical. It was synthesized by adopting and suitably modifying the protocol established by Blatt.[6] A mixture of 97 g of sodium nitrite ($NaNO_2$), 60 ml of methanol

(CH_3OH) and 212 ml of distilled water was added to a solution containing 51 ml of concentrated sulfuric acid (H_2SO_4; 96% purity) and 255 ml of distilled water. Both solutions were individually cooled to 0 ^{0}C and the acid was added dropwise to the nitrite and alcohol mixture. During the course of the reaction, the nitrite and alcohol mix was maintained at about -10 ^{0}C by utilizing a cold bath. A magnetic stirrer was used to prevent the reacting solutions from freezing. The methyl nitrite produced has a boiling point of -12 ^{0}C.[7] It was trapped at -78 ^{0}C, and subsequently transferred to a second similar cold trap in order to remove any impurities that might have been present. Despite the precautions, nitrous acid (HONO) remained as an impurity in the synthesized precursor. The Fourier Transform infrared spectrum of the gaseous precursor yielded infrared bands, which on comparison with Rook and Jacox's published spectra[8] showed features predominantly characteristic of methyl nitrite. The precursor was stored in liquid nitrogen until needed for the supersonic expansion.

Helium served as a carrier gas and was mixed with the synthesized precursor in the ratio 99:1 by volume. This premixed gas (at a typical pressure of 10 atm) was introduced into a vacuum chamber through a commercial pulsed valve [General Valve Iota One] with a 0.5 mm orifice. The open duration of the pulsed valve was set at

300 μs and the pressure in the evacuated chamber was typically 5 x 10^{-4} Torr. An excimer laser [Questek Series 2000] operating at 248 nm was used to photolyze the precursor close to the supersonic nozzle and the free radicals generated *in situ* in the jet were then probed with a YAG [Quanta Ray DCR-11]-pumped tunable dye laser [PDL-2]. The dye DCM [Exciton Chemical Co.] was used to produce the requisite range of wavelengths for the dye laser fundamental. A line-width of 0.2 cm^{-1} was obtained for the dye laser pulse and it could be narrowed to 0.05 cm^{-1} by incorporating an etalon in the resonator cavity. An autotracker [Quanta Ray WEX-1A] with a KDP crystal was employed to realize frequency-doubled wavelengths in the near ultraviolet so as to facilitate excitation of the molecular transitions.

A spatial separation of 10 - 12 mm was typically maintained within the jet between the excimer and dye laser pulses. The free radical fluorescence excited by the frequency-doubled dye laser probe was collected by a quartz lens in a direction orthogonal to the plane of the counterpropagating laser beams and the pulsed nozzle. A photomultiplier tube [EMI 9658R] was used to detect the total fluorescence. Laser excitation spectra of the OH and CH_3O radicals were obtained by scanning the wavelength of the dye laser. The signal was accumulated and averaged by a boxcar integrator [PAR 160] with a gate-width of 0.5 μs in conjunction with an IBM/XT microcomputer-aided data acquisition system.

In order to calibrate the frequency scale precisely, the absorption spectrum of molecular iodine (I_2) was recorded simultaneously with the dye laser fundamental while obtaining the OH and CH_3O spectra with the frequency-doubled output of the probe laser. An 1.2 m long iodine cell was maintained at room temperature for the purpose and employed in the double-pass mode to record the well-known B $^3\Pi^+_{ou}$ - X $^1\Sigma^+_g$ electronic system of I_2 in absorption.[9]

Results and Discussion

The CH_3O molecule belongs to the point group C_{3v}. Its ground electronic state $\tilde{X}\ ^2E$ is two-fold degenerate and is expected to split into $^2A'$ and $^2A''$ states.[10] The first excited electronic state of CH_3O is $\tilde{A}\ ^2A_1$ and the optical transition $\tilde{A}\ ^2A_1$ - $\tilde{X}\ ^2E$ remains the preferred choice for its detection. We have investigated the region of the 3^1_0 band of the $\tilde{A}$ - $\tilde{X}$ electronic system of the jet-cooled CH_3O radical in the vicinity of 32305 cm^{-1} where the A $^2\Sigma^+$ - X $^2\Pi_i$ (0,0) band of the OH radical[5] is also observed.

The frequency-doubled dye laser was tuned initially in the absence of the etalon and the LIF excitation

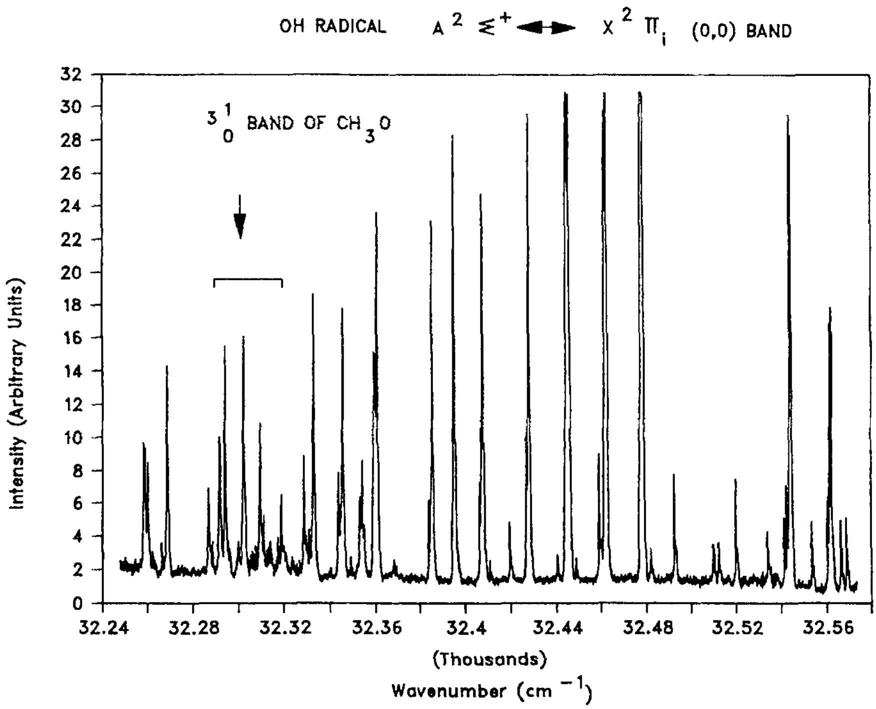

Fig. 1. Laser induced fluorescence excitation spectrum in the 32240 - 32580 cm^{-1} spectral region obtained in a supersonic jet expansion showing the intense peaks arising from the A - X (0,0) band system of the OH radical overlapping the much weaker $\tilde{A}$ - $\tilde{X}$ 3^1_0 band of the CH_3O radical.

spectrum recorded under low resolution. Figure 1 displays the 32240 - 32580 cm^{-1} spectral region showing intense rotational transitions corresponding to the A - X (0,0) band system of OH overlapped by the much weaker 3^1_0 band of the $\tilde{A}$ - $\tilde{X}$ system of CH_3O. A time delay of 6 μs was

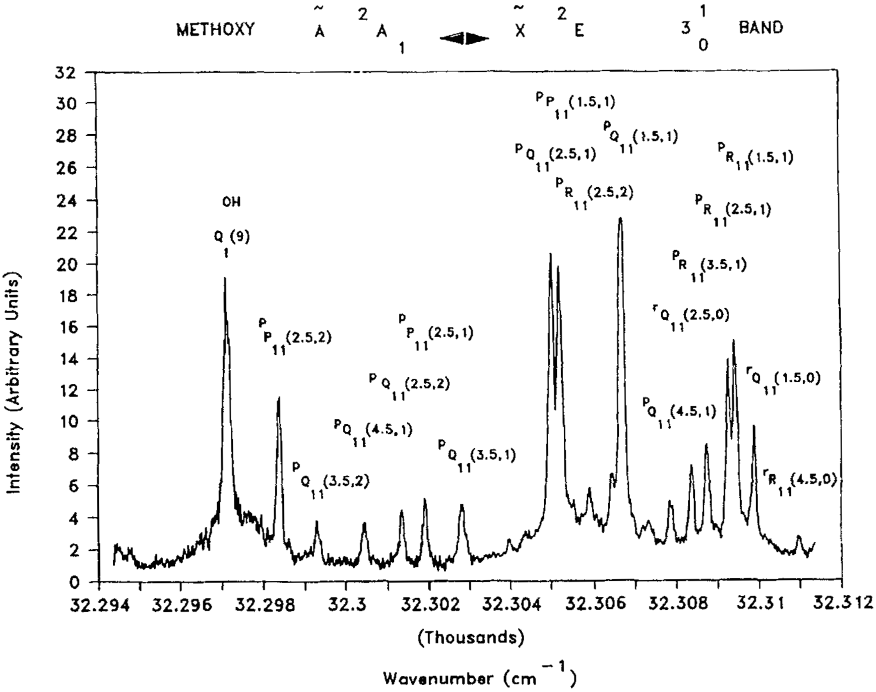

Fig. 2. High resolution laser induced fluorescence excitation spectrum of the $\tilde{A}$ - $\tilde{X}$ 3^1_0 band of the jet-cooled CH_3O radical showing assigned rotational transitions in the 32294 - 32312 cm^{-1} spectral region. A strong transition $Q_1(9)$ arising from the overlapping A - X (0,0) band of the OH radical is also labeled.

introduced between the photolysis and probe lasers to record the spectrum shown in Fig. 1. Once the low resolution spectrum had been obtained, the dye laser was tuned with the etalon in place and the high resolution rotationally-resolved spectrum of CH_3O was recorded in the 32294 - 32312 cm^{-1} region and is shown in Fig. 2. A combination of long pass colored filters [Oriel Corp. #59459 and Corning #0-53] helped cut-off the OH fluorescence and allowed LIF from CH_3O to be collected without interference. The absorption spectrum of I_2 was simultaneously obtained under high resolution in the 16147 - 16156 cm^{-1} domain utilizing the dye laser fundamental. An atlas[9] was used to identify the molecular iodine transitions belonging to the B $^3\Pi^+_{ou} \leftarrow$ X $^1\Sigma^+_g$ electronic system. A non-linear least squares fitting routine used the known iodine transitions to generate precise line positions for the rotational transitions corresponding to the 3^1_0 band of methoxy. Treating CH_3O as a prolate symmetric top molecule,[11] the (J,K) rotational assignments were made following the earlier work of Liu et al [4] Table 1 summarizes the rotational transitions identified and assigned to the $\tilde{A}\ ^2A_1$ - $\tilde{X}\ ^2E$ 3^1_0 band of CH_3O. The spectral branches indicated in Fig. 2 and Table 1 have been designated on the basis of the nomenclature developed by Herzberg[11] and Brown[12] for prolate symmetric top transitions in spin doublet states. The ΔJ character of the rotational transition is specified by primary symbols P, Q, and R, corresponding to ΔJ = -1, 0, +1, respectively. A superscript p recognizes the ΔK = -1 sub-band, whereas a superscript r

Table 1

Methoxy $\tilde{A}\ {}^2A_1 \rightarrow \tilde{X}\ {}^2E\ 3^1_0$ Band Rotational Transitions[a]

Wavenumber cm^{-1}	Transition
32298.39	${}^{p}P_{11}(2.5,2)$
32298.39	${}^{p}P_{11}(3.5,1)$
32299.28	${}^{p}Q_{11}(3.5,2)$
32300.41	${}^{p}Q_{11}(4.5,1)$
32301.31	${}^{p}Q_{11}(2.5,2)$
32301.89	${}^{p}P_{11}(2.5,1)$
32302.80	${}^{p}Q_{11}(3.5,1)$
32304.83	${}^{p}Q_{11}(2.5,1)$
32305.01	${}^{p}P_{11}(1.5,1)$
32305.68	${}^{p}R_{11}(2.5,2)$
32306.47	${}^{p}Q_{11}(1.5,1)$
32307.68	${}^{p}R_{11}(4.5,1)$
32308.24	${}^{r}Q_{11}(2.5,0)$
32308.64	${}^{p}R_{11}(3.5,1)$
32309.20	${}^{p}R_{11}(2.5,1)$
32309.39	${}^{p}R_{11}(1.5,1)$
32309.88	${}^{r}Q_{11}(1.5,0)$
32309.88	${}^{r}R_{11}(5.5,0)$
32311.13	${}^{r}R_{11}(4.5,0)$

[a] Experimental uncertainty in the measured wavenumbers is estimated to be 0.10 cm^{-1}.

labels the $\Delta K = +1$ sub-band. In addition, subscripts attached to the primary symbol help characterize the spin-rotation nature (F_1 or F_2) of a particular rotational transition. The spin-rotation component F_1 corresponds to the value $J = N + \frac{1}{2}$, while F_2 corresponds to $J = N - \frac{1}{2}$. Of the two subscripts associated with the primary symbol, the first refers to the upper electronic state ($\tilde{A}\ {}^2A_1$) and the second characterizes the lower electronic state ($\tilde{X}\ {}^2E$). Thus, for example, a particular transition ${}^PP_{11}(1.5,1)$ located at 32305.01 cm^{-1}, and shown in Fig. 2 and Table 1, has F_1 character in both states and has been assigned with $\Delta J = -1$, $\Delta K = -1$. The numbers in parentheses (1.5,1) are the rotational quantum numbers $J = 1.5$ and $K = 1$ and refer to the lower ${}^2E$ state. For the upper ${}^2A_1$ state, because the spin-rotation doublet is unresolved and degenerate,[4] the transitions $Q(J,K,F_1)$ and $P(J,K,F_2)$ cannot be distinguished and have the same transition frequency. Similar arguments apply to the pair of degenerate transitions $R(J,K,F_1)$ and $Q(J,K,F_2)$. In such cases, only one of the two rotational transitions is identified in Table 1 and labeled in Fig. 2. A strong OH transition, $Q_1(9)$ at 32297.38 cm^{-1}, was also identified[5] in the wavenumber span 32294 - 32312 cm^{-1} and is shown in Fig. 2.

The accurate line positions reported here for the rotational transitions in the 32294 - 32312 cm^{-1} region for CH_3O can be used together with the spectroscopic data from earlier investigations[4,13] to obtain precise molecular parameters for both the ground state $\tilde{X}\ {}^2E$ and the first excited state $\tilde{A}\ {}^2A_1$. Such molecular constants characterizing the electronic states are of considerable significance because of the strong theoretical and experimental interest in the spectroscopy of the methoxy radical.

Acknowledgments

Financial support from the Wright-Patterson Air Force Base (Grant# F33615-90-C-2038) and the National Aeronautics and Space Administration Center for the Study of Terrestrial and Extraterrestrial Atmospheres (Grant# NAGW-2950) is gratefully acknowledged.

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Date Received: 09/04/92
Date Accepted: 09/30/92