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Publisher *Taylor & Francis*

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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

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To cite this Article Misra, Prabhakar , Zhu, Ximming and Nur, Abdullahi H.(1992) 'Laser Induced Fluorescence Spectroscopy of the Hydroxyl Radical', *Spectroscopy Letters*, 25: 4, 547 — 557

To link to this Article: DOI: 10.1080/00387019208021529

URL: <http://dx.doi.org/10.1080/00387019208021529>

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**LASER INDUCED FLUORESCENCE SPECTROSCOPY
OF THE HYDROXYL RADICAL**

Key Words: Fluorescence, UV Spectroscopy, Hydroxyl Radical, Supersonic Jet.

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ABSTRACT

The hydroxyl radical has been generated by the excimer laser photolysis of nitrous acid at 248 nm. Rotationally-resolved excitation spectra in the wavenumber range $32170 - 32745 \text{ cm}^{-1}$ of the hydroxyl (OH) radical obtained by the Laser Induced Fluorescence (LIF) technique have been assigned. The excitation spectra have been recorded both for a static precursor and a supersonic jet expansion. Jet-cooled spectra of the OH radical exhibit rotational cooling and allow comparison with the static cell spectra in terms of population distributions of low-lying rotational levels.

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INTRODUCTION

The hydroxyl radical is an ubiquitous presence in combustion flows and flames and is a significant reactant in the earth's atmosphere. The ground state of the hydroxyl (OH) radical is $X^2\Pi$. The first electronic transition $A^2\Sigma^+ - X^2\Pi$, has been extensively studied both in absorption and in emission [1,2]. The formation of nitrous acid (HONO) has been proposed in the lower and upper atmosphere [3], primarily as a consequence of a three-body combination process of OH radicals with nitric oxide (NO):



where M is a third body. It is widely accepted that photolytic dissociation is a major sink for HONO:



The OH radicals, in turn, can react with HONO to yield H_2O and NO_2 :



Thus, the atmospheric chemistry of nitrous acid is dominated by two competing sink processes, namely its photolysis by solar radiation in the wavelength range 200 - 400 nm and its destruction by OH radicals. In the present investigation, the upper levels of the hydroxyl radical have been probed by laser induced fluorescence (LIF) at room temperature employing a static cell and at low temperatures by using a pulsed supersonic expansion.

EXPERIMENTAL

Nitrous acid (HONO) was the precursor for the hydroxyl (OH) radical. For the synthesis of HONO, two solutions were prepared. The first solution comprised of

a mixture of 25 g of sodium nitrite (NaNO_2) and 75 ml of distilled water (H_2O), while the second solution was dilute sulfuric acid prepared by mixing 50 ml of concentrated sulfuric acid (H_2SO_4) with distilled water (1:1 by volume). Both solutions were cooled to 0 $^{\circ}\text{C}$. The dilute acid was added dropwise to the sodium nitrite and water mixture. During the reaction, the nitrite and water mixture was maintained at about - 10 $^{\circ}\text{C}$ employing a cold bath. A magnetic stirrer was used to prevent the reacting solutions from freezing. The product, HONO, was trapped at - 78 $^{\circ}\text{C}$, and transferred to a second trap at the same temperature in order to minimize the presence of impurities, and then stored in liquid nitrogen.

The OH radical was produced by the excimer laser (KrF at 248 nm) photolysis of HONO. The OH radical was subsequently excited by a tunable dye laser. Fluorescence excitation spectra were obtained by scanning the dye laser. Two kinds of LIF experiments were done. In one series of experiments, the reaction chamber was filled with HONO precursor at a typical pressure of 10 mtorr. In the second series of experiments, helium was mixed with HONO in the ratio 99:1 by volume and then introduced at high pressures (typically 10 atmospheres) into the reaction chamber through a commercial pulsed valve [General Valve IOTA ONE] with a 0.5 mm orifice. The open duration of the valve was set at 300 μs , while the pressure in the evacuated chamber was of the order of 5×10^{-4} torr.

An excimer laser [Questek 2000] beam at 248 nm was focused into the chamber by a quartz lens of focal length 75 cm. The focal spot was set as close to the nozzle as possible. The absorption cross-section of nitrous acid (HONO) at 248 nm is $2 \times 10^{-19} \text{ cm}^2$ [4]. The exciting beam

was generated by a tunable dye laser [Quanta Ray PDL-2] that was pumped by the second harmonic (at 532 nm) of a Nd:YAG laser [Quanta Ray DCR-11]. Organic dyes KR620 and Rh640 [Exciton Chemical Co.] were used in the dye laser circulator. Frequency-doubling was accomplished by a KDP crystal in conjunction with an autotracker [Quanta Ray WEX-1A]. The ultraviolet dye laser pulses excited the OH radicals downstream from the photolysis laser, corresponding to time delays between the two lasers that ranged typically from 1 to 9 μ s. The laser-induced fluorescence was collected with the help of a quartz lens at right angles to the plane of the counterpropagating laser beams and the nozzle. Total fluorescence was detected by a photomultiplier tube [EMI 9658R]. The signals were accumulated with a boxcar integrator [Princeton Applied Research 160] with a typical gate-width of 0.5 μ s and an IBM/XT microcomputer-aided data acquisition system. An iodine absorption cell of length 1.2 m in the double-pass mode was used at room temperature to calibrate the excitation frequency.

RESULTS AND DISCUSSION

Figure 1 is an illustration of the rotationally - resolved LIF excitation spectrum and the assignment of the (0,0) band of the A-X system of OH obtained in the cell at a pressure of 10 mtorr. Eight branches can be clearly seen and are labeled. The relative intensities of the rotational transitions can be understood on the basis of the populations of the various rotational energy levels corresponding to the vibrational states. The fact that the spacing of the rotational lines is not constant can be attributed to coupling between the rotational and vibrational motions of the OH molecule.

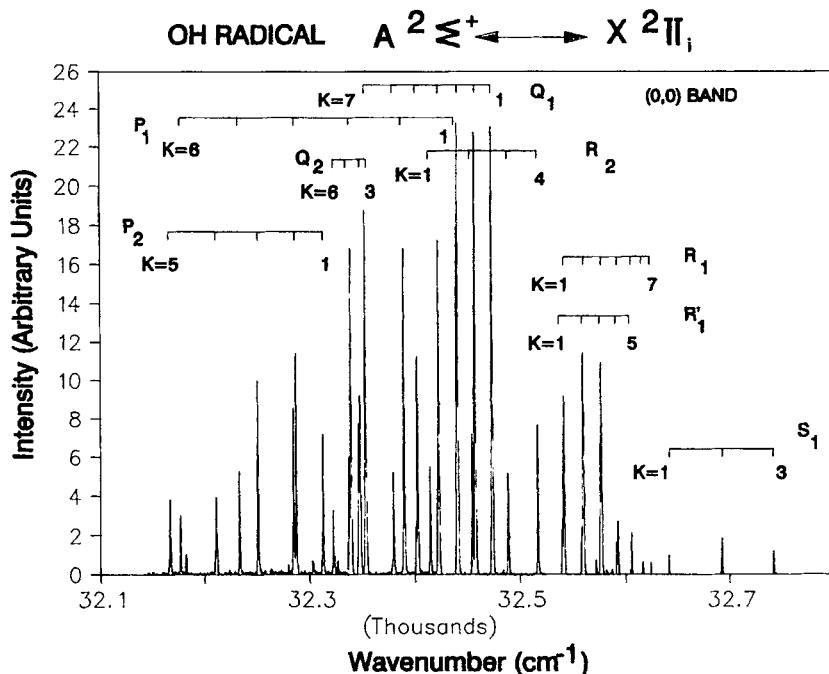


FIG. 1. Rotationally-resolved laser-induced fluorescence excitation spectrum of the (0,0) band of the A-X system of OH obtained in the cell at a pressure of 10 mtorr.

When there is statistical equilibrium in the fluorescence source and, therefore, a temperature exists, the intensity distribution may be used to determine the gas temperature. The intensity of a line due to a transition $j \rightarrow i$ is given by $I_{ji} = N_j A_{ji} h\nu_{ji}$, where N_j specifies the number of molecules in the initial state j , A_{ji} is the transition probability for the transition $j \rightarrow i$, and ν_{ji} is the transition frequency. For temperature equilibrium, if the levels are not degenerate, $N_j = N_0 \exp(-E_j/kT)$, where N_0 is a constant, E_j the energy of the state j , T the absolute temperature,

and k the Boltzmann constant. For degenerate states, N_j specifies the number of molecules in each substate. The transition probabilities A_{ji} are then obtained by summing over the transitions between the individual substates. Temperature equilibrium exists when the foregoing exponential expression for $N_j(T)$ holds, in general, for all energies including translational, rotational, vibrational and electronic. If the above equation for N_j is valid for rotational energies, we speak of a rotational temperature T_R . When there is general temperature equilibrium, as is the case for static cell LIF measurements for the OH radical, the rotational temperature is equal to the gas temperature.

For an electronic transition, like the one we are considering here, the absolute line frequency is given by $\nu = \nu_e + \nu_v + \nu_r$, where ν_e , ν_v , and ν_r , refer to the contributions due to electronic, vibrational, and rotational motions, respectively. The quantity $\nu_0 = \nu_e + \nu_v$ is constant for a specific vibrational transition and is called the band origin. The band origin ν_0 for the A-X (0,0) band of OH is located at 32402.1 cm^{-1} [5].

In addition to photolyzing the precursor HONO diluted with helium by an excimer laser in the cell, a pulsed supersonic jet expansion of high pressure helium seeded with HONO was photodissociated with excimer laser pulses at 248 nm. In general, the photolysis of HONO in a free jet will deposit large amounts of energy into the vibrational and rotational degrees of freedom of the molecular products. This energy, in turn, can be transferred to the cold carrier gas via two-body collisions. The rate of such secondary cooling is dependent upon the collision rate. The temperature of the

photofragments can be controlled by varying the number of collisions they suffer with the carrier gas. This can be achieved either by changing the distance between the nozzle and the photolysis region or by varying the distance between the photolysis and probe lasers, and by altering the stagnation pressure of the gas reservoir [6].

The timing of the photolysis and probe lasers is crucial to the LIF experiments. Time delay between the firing of the photolysis laser and the probe laser is precisely controlled in order to successfully detect the OH fragments as they move through the region probed by the tunable dye laser. This overall timing is determined from the stream velocity of the helium expansion, which is $1.78 \times 10^5 \text{ cm s}^{-1}$ [6]. If the two lasers are focussed to points well separated in the jet, the resultant LIF spectra will be vibrationally and rotationally cold. As the lasers are moved towards each other, the spectra will become progressively warmer.

Figures 2 and 3 display excitation spectra for the A-X (0,0) band of OH recorded at a helium backing pressure of 9 atmospheres and with time delays 1.5 and 6.0 μs , respectively, between the photolysis and probe lasers. A comparison of the two spectra clearly shows rotational cooling for the OH transitions in case of the longer time delay. In addition, if these two jet spectra are compared with the cell spectrum shown in Fig. 1, it becomes apparent that the jet affords greater rotational cooling than the static sample in the cell.

Spectral assignments of the rotational transitions were made using appropriate energy levels of OH and

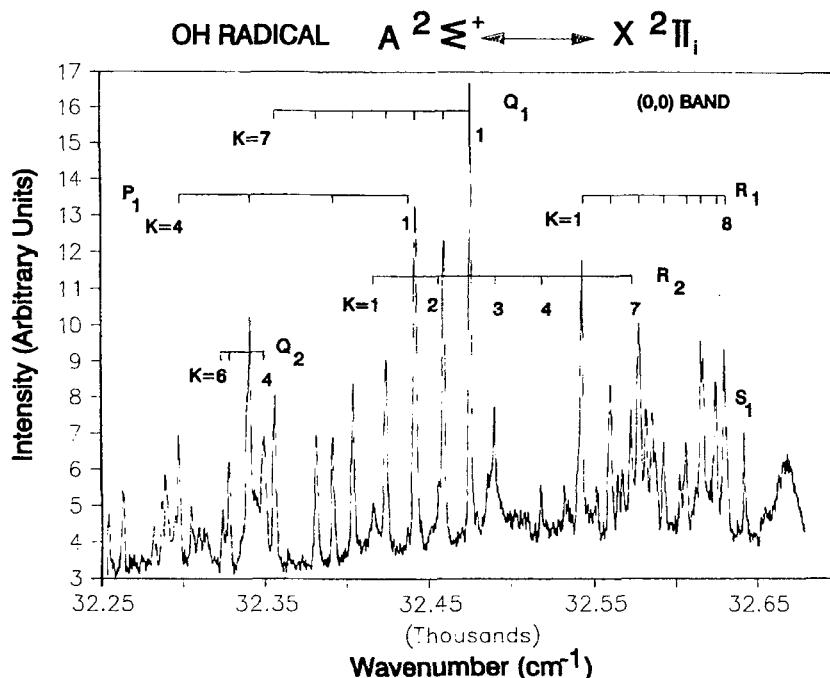


FIG. 2. Excitation spectrum of the (0,0) band of the A-X system of OH obtained in the supersonic jet at a helium backing pressure of 9 atm. The time delay between the photolysis and probe lasers was 1.5 μs .

follow those by Dieke and Crosswhite [2]. Table 1 summarizes all of the assigned transitions for the $A^2\Sigma^+ - X^2\Pi_g$ (0,0) band of OH. The main branches P_1 , P_2 , Q_1 , Q_2 , R_1 , R_2 and S_1 are clearly resolved and labeled in Fig. 1. A satellite branch R_1' is seen red-shifted from the main branch R_1 . A comparison of the jet-cooled spectra with the cell spectra shows that the Q_1 branch is the strongest observed branch in either case. However, the R_2 branch is drastically reduced in intensity relative to the Q_1 branch in the jet expansion as compared to the

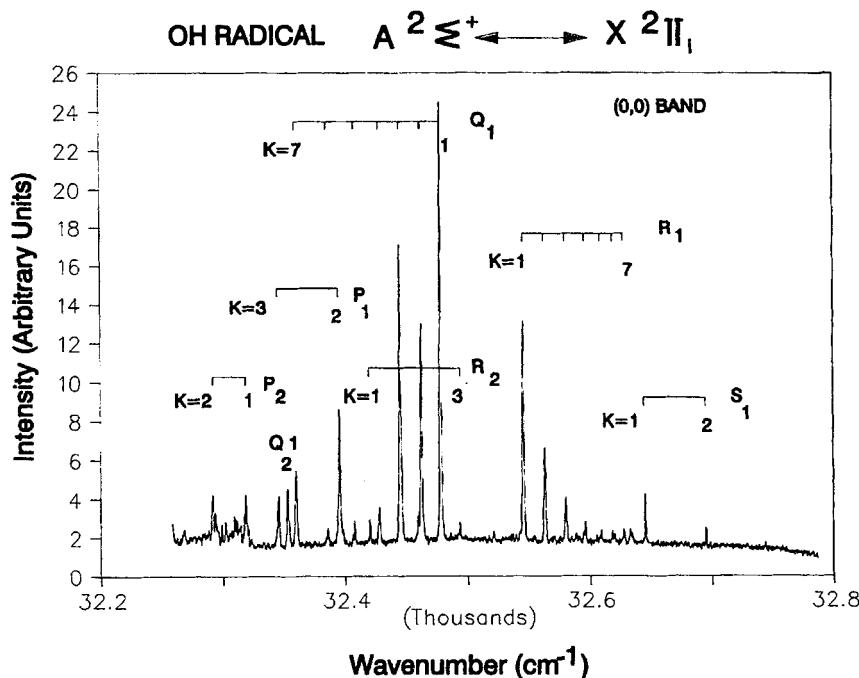


FIG. 3. Excitation spectrum of the (0,0) band of the A-X system of OH obtained in the supersonic jet at a helium backing pressure of 9 atm. The time delay between the photolysis and probe lasers was 6.0 μs .

cell. These observations can be understood in terms of reduced populations in the $J = K - (1/2)$ rotational levels as compared to the $J = K + (1/2)$ levels for the OH radical in the jet as compared to the cell. Here J and K are the quantum numbers for the total angular momentum and the angular momentum apart from spin, respectively. The branches as seen in the jet (Fig. 3) drop off in intensity rapidly for increasing K values, especially after $K = 3$. This intensity decrease is much more gradual for the branches observed in the cell (Fig. 1) and

TABLE 1

ROTATIONAL TRANSITIONS OF OH A $^2\Sigma^+$ - X $^2\Pi_g$ (0,0) BAND

| Wavenumber (cm $^{-1}$) | Transition | Wavenumber (cm $^{-1}$) | Transition |
|-----------------------------|------------------------------------|-----------------------------|-------------------|
| 32170.4 | P ₂ 5 | 32440.6 | P ₁ 1 |
| 32180.8 | P ₁ 6 | 32441.9 | Q ₁ 3 |
| 32214.0 | P ₂ 4 | 32455.7 | R ₂ 2 |
| 32236.0 | P ₁ 5 | 32458.6 | Q ₁ 2 |
| 32253.0 | P ₂ 3 | 32474.6 | Q ₁ 1 |
| 32286.8 | P ₂ 2 | 32489.5 | R ₂ 3 |
| 32289.1 | P ₁ 4 | 32517.6 | R ₂ 4 |
| 32314.2 | P ₂ 1 | 32542.0 | R ₁ 1' |
| 32324.0 | Q ₂ 6 | 32546.2 | R ₁ 1 |
| 32338.9 | Q ₂ 5 | 32559.5 | R ₁ 2' |
| 32340.7 | P ₁ 3 | 32560.5 | R ₁ 2 |
| 32348.2 | Q ₂ 1 | 32576.6 | R ₁ 3' |
| 32349.3 | Q ₂ 4 | 32577.6 | R ₁ 3 |
| 32354.5 | Q ₂ 2, Q ₂ 3 | 32591.9 | R ₁ 4' |
| 32355.9 | Q ₁ 7 | 32593.2 | R ₁ 4 |
| 32381.0 | Q ₁ 6 | 32606.6 | R ₁ 5 |
| 32391.0 | P ₁ 2 | 32617.5 | R ₁ 6 |
| 32403.5 | Q ₁ 5 | 32625.6 | R ₁ 7 |
| 32415.5 | R ₂ 1 | 32643.4 | S ₁ 1 |
| 32423.6 | Q ₁ 4 | 32694.6 | S ₁ 2 |
| | | 32744.6 | S ₁ 3 |

manifests itself appreciably after $K = 6$. Such a comparison proves clearly the cooling effect of the supersonic expansion. It indicates that, for the specified experimental conditions, the populations of the OH molecules in rotational levels above $K = 3$ are significantly reduced in the jet over that in the cell.

ACKNOWLEDGMENTS

The research work reported here was supported by Wright-Patterson Air Force Base (Grant# F33615-90-C-2038), the Howard University Faculty Research Support Grant Program and the Collaborative Core Unit of the Graduate School of Arts & Sciences. We would like to thank Prof. Joshua B. Halpern for invaluable assistance in obtaining the spectra.

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Date Received: 12/04/91
Date Accepted: 01/08/92