LASER EXCITED SPECTRA OF THE JET-COOLED ETHOXY RADICAL

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Abstract

Extensive laser-excitation and dispersed fluorescence spectra of the jet-cooled ethoxy radical have been recorded and analyzed. Seven vibrational frequencies have been assigned for the excited \( \text{B}^2\text{A}^\prime \) electronic state and eight for the ground \( \text{X}^2\text{A}^\prime \) state.

Introduction

The ethoxy \((\text{C}_2\text{H}_5\text{O})\) radical has great theoretical and practical significance. It is a reactive intermediate in combustion and oxidation reactions involving hydrocarbons. It belongs to the \( \text{C}_s \) point group and has 18 vibrational frequencies.\(^1\) Four vibrational frequencies have been reported earlier by Inoue et al.\(^2\) and Ebata et al.\(^3\) but only one, namely the CO stretch, has been assigned definitively. Miller et al.\(^4\) have published the rotationally-resolved electronic excitation spectra of \( \text{C}_2\text{H}_5\text{O} \) for the C-O stretch mode involving the excited vibrational states with \( v^\prime = 0, 1, \) and \( 2 \). Analysis of the emission spectra of \( \text{C}_2\text{H}_5\text{O} \) is much more difficult as compared to methoxy \((\text{CH}_3\text{O})\), because not only is the Laser-Induced Fluorescence (LIF) signal much weaker, but also the dispersed spectra are more congested for the heavier ethoxy 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 analyzer 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 \( \text{B}^2\text{A}^\prime \) state and eight frequencies for the ground \( \text{X}^2\text{A}^\prime \) state. To the best of our knowledge, of the assigned vibrational frequencies, ten (six for the excited \( \text{B} \) state and four for the ground \( \text{X} \) state) are being reported for the first time. In addition, vibrational and anharmonic constants have been obtained via least-squares fits for the C-O stretch \((v_{10})\) mode for both the ground \( \text{X} \) state and the excited \( \text{B} \) state.

Experimental

The precursor used for generating the ethoxy radical was ethynitrite \((\text{C}_2\text{H}_5\text{ONO})\). It was synthesized\(^6\) using a mixture of sodium nitrite \((\text{NaNO}_2\)) and ethyl alcohol \((\text{C}_2\text{H}_5\text{OH})\) and dropwise addition of sulfuric acid \((\text{H}_2\text{SO}_4)\). Freshly synthesized \(\text{C}_2\text{H}_5\text{ONO}\) 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-ethyl nitrite mixture (at a typical pressure of 14 atm.) was introduced into a vacuum chamber through a pulsed valve \(\text{[General Valve IOTA ONE]}\) with a 0.5 mm orifice. With the open duration of the pulsed valve set at 200 us, a typical pressure in the expansion chamber was \(1 \times 10^4\) Torr. Ethyl nitrite seeded in the supersonic jet expansion was
photolyzed by KrF laser pulses at 248 nm from an excimer laser [Questek Impulse 4530]. The C\textsubscript{2}H\textsubscript{2}O molecules generated \textit{in situ} were excited by a tunable dye laser [Spectra Physics PDL-3] that was frequency-doubled using 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 the lasers and the pulsed valve were run at 10 Hz. The separation between the photolysis and excitation lasers was typically 10-12 mm and the delay between the two lasers was maintained around 8 us. A nominal linewidth of 0.07 cm\textsuperscript{-1} was estimated for the dye pulse used to record the excitation spectrum of the ethoxy radical. Laser-induced fluorescence from the excited ethoxy molecules 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. \textit{Optogalvanic} transitions excited within a hollow cathode Fe-Ne lamp\textsuperscript{7} were used to obtain accurate wavelength calibration of the laser excitation spectra. An optical multichannel analyzer system [EG & G Princeton Applied Research OMA-4] was employed to record wavelength-resolved emission spectra of the ethoxy radical. The OMA system included a 0.275 m spectrograph [Acton Research Corp. SpectraPro 275], a lens-coupled intensifier, a 256 x 1024 element CCD array cooled to -120 °C and a data processor. The resolution of the dispersed fluorescence spectra recorded was about 23 cm\textsuperscript{-1} in the near UV and visible regions.

\textbf{Results}

A composite laser excitation spectrum of the ethoxy radical in the region 29,100-32,200 cm\textsuperscript{-1} is illustrated in Fig. 1. Our vibronic analysis focused on the \(B^2\)A' - X \(\widetilde{X}^2A''\) transition. The excitation spectrum for ethoxy showed a dominant progression with vibrational spacings decreasing from 603 to 580 cm\textsuperscript{-1} owing to anharmonicity, which was assigned to the C-O stretch mode. The first member of this vibrational progression at 29181 cm\textsuperscript{-1} was assigned as the \(0^0\) band as indicated in Fig. 1. Six additional progressions with smaller amplitudes were found located at 29425, 29543, 30050, 30074, 30504 and 30641 cm\textsuperscript{-1}, respectively. We have identified and assigned these spectral features as bands involving modes that are in combination with the the C-O stretch mode. A comprehensive analysis of all of the observed bands in excitation has enabled the assignment of seven vibrational frequencies for the excited \(B^2\)A' state, namely 1460 cm\textsuperscript{-1} for CH\textsubscript{2} scissors, 1323 cm\textsuperscript{-1} for CH\textsubscript{2} wag, 896 cm\textsuperscript{-1} for CC stretch, 603 cm\textsuperscript{-1} for CO stretch, 362 cm\textsuperscript{-1} for CCO deformation, 893 cm\textsuperscript{-1} for CH\textsubscript{2} rocking and 244 cm\textsuperscript{-1} for torsion, respectively.

All of the bands associated with the vibrational modes recorded in excitation showed similar structure, except the bands involving the the CH\textsubscript{2} rocking and torsion modes. As per symmetry classification of symmetric tops of C\textsubscript{2} symmetry,\textsuperscript{8} the 18 vibrational modes of the C\textsubscript{2}H\textsubscript{2}O molecule can be divided into two groups of symmetry \(a'\) and \(a''\). Bands belonging to the two different symmetry species (a' or a'') were observed to have clearly different spectral appearance and rotational structure.

A typical dispersed fluorescence spectrum of the jet-cooled ethoxy radical is displayed in Fig. 2. It shows wavelength-resolved emission when the 10\(\nu_0\) band is pumped. As expected, the

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CO-stretch mode is the most active vibrational mode in dispersed fluorescence. Exhibiting behavior similar to the excitation spectra, there are progressions involving the ground state with intervals corresponding to the CO-stretch that are built on different distinct frequencies, and these have been assigned to be combinations bands. The distinct frequencies determined for the $X^2A^+$ state have been assigned to the CH$_2$ s-stretch (2753 cm$^{-1}$), the CC stretch (910 cm$^{-1}$), the CO stretch (1068 cm$^{-1}$), the CCO deformation (444 cm$^{-1}$), the CH$_2$ twist (1277 cm$^{-1}$), the CH$_3$ rock (984 cm$^{-1}$), the CH$_2$ rock (943 cm$^{-1}$) and torsion (370 cm$^{-1}$) modes, respectively.

In conclusion, the laser excitation and dispersed fluorescence spectra of the ethoxy radical are characterized by prominent progressions involving the CO-stretch vibrational mode. An in-depth spectral analysis has allowed the determination of seven vibrational frequencies (namely, the CH$_2$ scissor, the CH$_3$ wag, the CC stretch, the CO stretch, the CCO deformation, the CH$_3$ rock and torsion modes) for the excited B'$^2A'$ state and eight vibrational frequencies (namely, the CH$_2$ s-stretch, the CC stretch, the CO stretch, the CCO deformation, the CH$_2$ twist, the CH$_3$ rock, the CH$_2$ rock and torsion modes) for the ground $X^2A^+$ state.

Acknowledgements

Financial support from the NASA Lewis Research Center (Grant No. NAG3-1677), the U.S. Environmental Protection Agency’s Office of Exploratory Research (Grant No. R819720-01-2), and the Center for the Study of Terrestrial and Extraterrestrial Atmospheres (Grant No. NASA NAGW-2950) is gratefully acknowledged.

References

Fig. 1. Laser excitation fluorescence spectrum of the \( B^2\text{A}' - X^2\text{A}'' \) system of the ethoxy radical. The time delay between the excimer laser and the dye laser was 8 µs.
Fig. 2. The dispersed spectrum of the B-X $10_0^3$ band of the ethoxy radical. The frequency of the pump laser was 30972 cm$^{-1}$ and the time delay between the excimer and dye lasers was 5 μs.