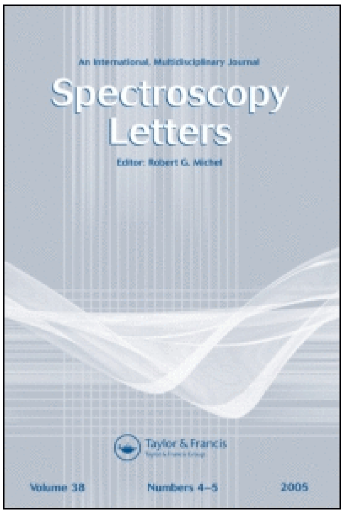

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Collisional Deactivation of Laser Induced Ethylene Fluorescence Lifetime of Vibrationally Excited Ethylene in Air at Atmospheric Pressure

James W. Robinson[a]; James D. Dake[a]
[a] Department of Chemistry, Louisiana State University Baton Rouge, Louisiana

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COLLISIONAL DEACTIVATION OF LASER INDUCED ETHYLENE FLUORESCENCE
LIFETIME OF VIBRATIONALLY EXCITED ETHYLENE IN AIR AT ATMOSPHERIC PRESSURE

James W. Robinson and James D. Dake
Department of Chemistry
Louisiana State University
Baton Rouge, Louisiana 70803

I. INTRODUCTION

Laser induced infrared fluorescence[1,2] is a potential method for the remote detection of atmospheric pollutants.[3,4] In evaluating this technique as a quantitative analytical tool, two important parameters are (a) the lifetimes of the excited species and (b) the quenching efficiencies of various molecules which would be expected to be in the atmosphere and which may collide with the excited species. Such quenching would lead to low fluorescence intensity and low analytical data. We have measured the quenching of the fluorescence of ethylene, which is a common hydrocarbon pollutant, by nitrogen, nitrogen saturated with water vapor, and air.

Millikan has reported that water vapor is a very efficient quencher of carbon monoxide vibrational fluorescence,[5] and since water vapor is found in relatively large concentrations in the atmosphere its ability to quench ethylene fluorescence was of considerable interest. It was found that the quenching effects were not great and should not present a significant analytical problem. It was shown that major changes in humidity would not cause significant changes in fluorescence intensity.

From the quenching data and from recently published lifetime data for ethylene at reduced pressures,[6] we calculated the lifetime of vibrationally excited ethylene in air at atmospheric pressure. From this lifetime the depth resolution of a hypothetical remote pollution monitor was calculated.

II. EXPERIMENTAL

A. Equipment

1. Laser -- A continuous CO_2 gas laser was used as the excitation source. The laser was tuned to 10.6 μ by a diffraction grating which served as the rear reflector of the laser. The laser produced approximately 8 watts in a beam one cm in diameter. The power varied less than 5% during the experiments.

2. Chopper -- A Princeton Applied Research, Model 125, Mechanical Chopper was used to modulate the laser beam at 13 Hz.

3. Fluorescence Cell -- A glass cell 20 cm long and 4 cm in diameter was used to contain the gas samples. Irtran-2 (Eastman Kodak) was used for the laser beam entrance and exit windows and for the fluorescence exit window. Gas pressures inside the cell were measured with a metal diaphragm vacuum gauge.

4. Filter System -- A McPherson, Model 607, Filter Assembly was used to limit the radiation striking the detector to the 7 to 14 micron region.

5. Detector -- A Barnes Engineering pyroelectric detector was used.

6. Amplifier -- A Princeton Applied Research, Model 124, lock-in amplifier and a PAR, Model 116, preamplifier were used.

7. Power Meter -- The laser power was monitored throughout the experiments with a Coherent Radiation, Model 201, Power Meter.

B. Gases Used

1. Ethylene -- Matheson Chemically Pure ethylene was used without further treatment.

2. Nitrogen -- Nitrogen source with a purity of 99.9 +% was used without further treatment.

3. Air -- Room air was used.

The optical arrangement is shown in Figure 1.

C. Experimental Procedure

The fluorescence cell was evacuated, flushed with ethylene and re-evacuated. Ethylene was then introduced into the cell, and the pressure adjusted to thirty-five torr. The fluorescence intensity then was measured.

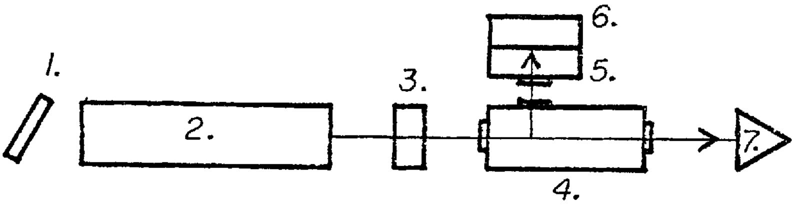
The fluorescence spectrum of ethylene[1] was reported in a previous publication. By using a 7-14 μ filter between the source and the detector the total radiation from the fluorescence bands at 7.2 μ and 10.6 μ were observed.

The intensity of scattered laser radiation inside the cell was much less than the fluorescence intensity, and was easily subtracted from the total signal.

After measuring the fluorescence intensity of the pure ethylene, various amounts of nitrogen, or nitrogen saturated with water vapor, or air were added to the cell. After each addition of the quenching gas, the pressure inside the cell and the fluorescence intensity were recorded. The quenching gases were added until atmospheric pressure was reached inside the cell.

III. RESULTS AND DISCUSSION

The fluorescence intensity of the pure ethylene divided by the fluorescence intensity after the addition of the quenching gas, $\frac{I_0}{I}$,



1. Grating
2. CO_2 Laser
3. Chopper
4. Fluorescence Cell
5. Filter Assembly
6. Detector
7. Power Meter

FIGURE 1. Optical Arrangement

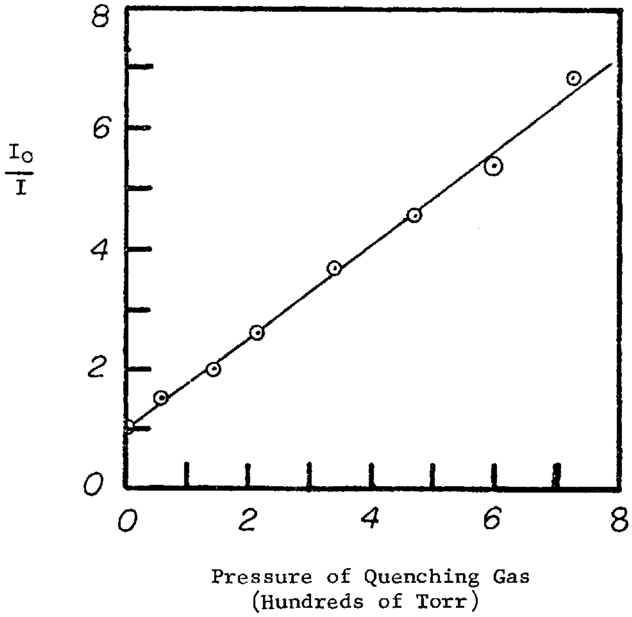


FIGURE 2. Quenching of Ethylene Fluorescence by Nitrogen

was plotted against the pressure of the gas added. Figure 2 shows the quenching of ethylene by nitrogen. Figure 3 shows the quenching by nitrogen saturated with water vapor. And Figure 4 shows the quenching by air. In each case the initial amount of ethylene was 35 torr.

From the plots it is apparent that the quenching efficiencies of the three components tested were small and that the efficiencies were about the same value. Nitrogen saturated with H_2O quenched the fluorescence slightly more than did dry nitrogen, and room air quenched slightly more efficiently than nitrogen saturated with water vapor.

The minor differences illustrated by Figures 2 and 3 between dry nitrogen and nitrogen saturated by water indicate that major changes in humidity would cause very little change in fluorescence intensity. Also in air samples it would be expected that the nitrogen concentration would remain reasonably constant.

This would not be true for stack gases where a correction for variation in N_2 may be necessary. The data illustrated in Figures 2 and 4 also indicate these wide variations in O_2 caused only minor effects on fluorescence intensity. No correction for oxygen variation may be necessary in stack gas monitoring data.

Using the Stern-Volmer quenching equation[6,7] the lifetime of excited ethylene in air at atmospheric pressure was calculated as follows.

$$\frac{I_o}{I} = \frac{\tau_o}{\tau_1}$$

Where τ_o if the lifetime of the fluorescence of the pure gas and τ_1 is the lifetime of the collisionally quenched fluorescence.

Yuan and Flynn have reported the lifetime of vibrationally excited ethylene at 35 torr to be 3.8 μ sec.[6] From the equation above, τ_1 was

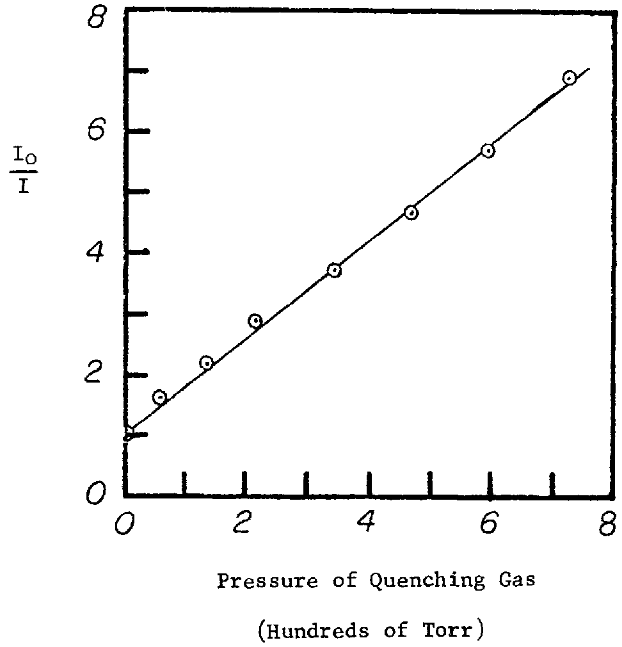


FIGURE 3. Quenching of Ethylene Fluorescence by Nitrogen Saturated with Water Vapor.

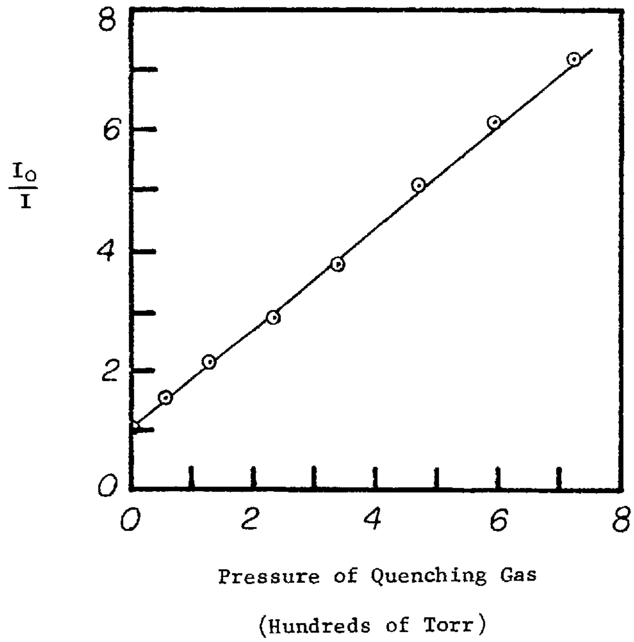


FIGURE 4. Quenching of Ethylene Fluorescence by Room Air

calculated to be 0.5 μ sec in air at atmospheric pressure. This lifetime corresponds to 5×10^3 collisions per excited ethylene molecule.

Using an approximation proposed by Kildal and Byer the range resolution of a remote monitoring device may be calculated.[4]

$$\Delta R \approx \frac{c}{2}(t_o + t_g + \tau)$$

Where ΔR is the range resolution, c is the speed of light, t_o is the laser pulse width, t_g is the gate width of the detection system, and τ is the lifetime of the fluorescent species. Assuming a laser pulse width of 200 n sec and a gate width of 50 n sec, the depth resolution to one significant figure is 100 m. This resolution is sufficient to permit range determinations of molecular pollutants when using a remote sensing apparatus.

IV. ACKNOWLEDGMENT

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V. SUMMARY

The collisional deactivation of laser induced ethylene fluorescence was measured for nitrogen, nitrogen saturated with water vapor, and air. From these measurements the lifetime of vibrationally excited ethylene in air at atmospheric pressure was calculated to be 0.5 μ sec. The depth resolution of a hypothetical remote monitoring device was calculated to be 100 meters. Results showed that the quenching effects were similar in all cases and in no case were they great. Major changes in humidity should not present an analytical problem in practice.

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