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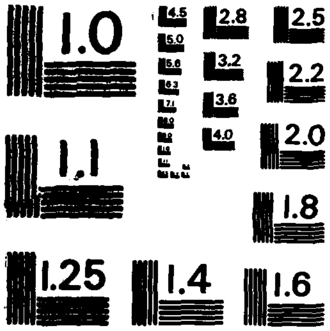

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# LASER SPECTROSCOPY OF OZONE

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18 December 1985

Final Report
1 July 1980 - 30 September 1985

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AIR FORCE GEOPHYSICS LABORATORY
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Data have been obtained for the first time on the fluorescence spectrum of ozone in the Hartley continuum region. This type of data provides information for a new kind of spectroscopy with hitherto unprecedented capabilities for studying both ground state vibrational structure and excited state dissociation dynamics. From this data and theoretical models, qualitative generalizations are made about the potential energy surface of the upper electronic state of the Hartley transition. Experiments have also been conducted to obtain the high resolution spectrum of some of the Huggins bands for jet-cooled ozone. An analysis of the partially resolved rotational structure of these bands indicates that the symmetry of the Huggins bands is the same as that for the Hartley continuum.

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## SUMMARY OF RESEARCH

This contract covered the period July 1, 1980 - September 30, 1985. The aim of the work was to improve understanding of the UV and visible spectrum of the atmospheric species $O_3$ and to improve knowledge of its vibrational levels in the molecule's ground electronic state. Ozone photodissociates readily on absorption of light at any wavelength longer than ~850 nm. Consequently, the absorption spectrum is entirely diffuse. There are three principal spectroscopic regions = The Chappuis band ($^1B_1 \leftarrow \tilde{X}^1A_1$,~λ450-850 nm), the Huggins band ($^1B_2 \leftarrow \tilde{X}^1A_1$, ~λ300-360 nm) and the Hartley band ($^1B_2 \leftarrow \tilde{X}^1A_1$, ~λ200-300 nm). The dominant and by far the most intense of these is the Hartley band, centered around ~λ255 nm. Because of the rapid predissociation in this region, the band is almost entirely featureless, though there is some very faint structure near the band center. To the red, the much weaker (by $\sim 10^{-3}$) Huggins system is also diffuse, but it exhibits definite vibrational structure.

The original idea of this work was to investigate the feeble structure in the Hartley band and the vibrational transitions in the Huggins band by looking at fluorescence excitation spectra of very cold ozone. The cooling (to ~10 K) was to be accomplished by adiabatic expansion of an ozone-helium mixture into a free-jet pulsed molecular beam. Our group already had some experience with $O_3$ molecular beams and tuneable UV laser spectroscopy.

## Introduction:

A summary of the research done for this contract is reported in this technical report. The detailed research results and the description of the experiments have been reported in the open literature and a listing of the journal articles is given in the Publication section of this report.

It is important to note that in the process of conducting laser experiments on ozone, fluorescence was unexpectedly observed when the laser was tuned to 266 nm which is in the peak absorption region of the Hartley continuum. This is surprising because it has always been assumed that the ozone is completely photodissociated in this wavelength region. Apparently, the laser light intensity is sufficiently strong that the small fraction of molecules that fluoresce is observable. This observation has led to a new kind of spectroscopy with unprecedented capabilities for studying excited state dissociation dynamics and ground state vibrational structure.

Shortly after the project started, these goals were expanded to include study of the resolved fluorescence of the photodissociating molecules. Inspired by theoretical ideas put forward by E. J. Heller and coworkers, we realized that such data could provide a new kind of spectroscopy with hitherto unprecedented capabilities for studying both ground-state vibrational structure and excited-state dissociation dynamics. The first measurements of this kind were made on ozone (in a static cell), and they revealed a sequence of vibrational levels in the ground electronic state reaching to within 500 $cm^{-1}$ of the molecule's dissociation limit. This was and remains a record for any polyatomic molecules.

The levels that could be assigned were all of the type $1_n 2_0 3_m$, i.e., no ground-state excited bending levels were observed. In the light of the Heller theory, this is a clear indication that dissociation on the upper potential energy surface proceeds with motion of the departing oxygen atom almost directly in the direction of the broken bond. Further qualitative generalizations were made about the shape of the excited-state potential in the Franck-Condon region. Specifically, it was concluded that the surface is saddle-shaped with respect to $q_1$(symmetric stretch) and $q_3$ (antisymmetric stretch). This confirmed the idea that the weak structure in the Hartley band probably occurs because there are a few oscillations in the $q_1$ coordinate before the motion accelerates in the $q_3$ direction leading to dissociation. A more quantitative theoretical treatment has not yet been completed, but such a study is planned for the future. Later work also revealed a very small intensity into the $2_1$ level (~1% of that into $1_1$). The quantitative remeasurement of the whole $O_3$ emission spectrum, with special attention to such minor features, will be an important step in the continuation of our studies on ozone.

A theoretical model for the stretching vibrations of ozone, based on a completely algebraic Hamiltonian, was completed in collaboration with Professor R. D. Levine. It was found that the algebraic approach could fit the observed levels competitively with conventional (Darling-Dennision) methods, yet retain a consistent anharmonic-oscillator perspective. Darling-Dennison analysis mixes harmonic and anharmonic expressions.

Subsequent experimental work turned more towards the original idea, but focussed on the weak Huggins system instead of the Hartley band. A pulsed nozzle beam appropriate for these studies was developed and tested. At about this time, we also started considering whether some sort of optical multichannel analyzer could be found so that we could record an entire wavelength region simultaneously rather than by tedious scanning from line to line. Because of the extremely low light levels inherent in these experiments, it quickly became clear that the readout error would swamp the signal without at least two stages of amplification (image enhancement). Eventually, a unit that seemed suitable was identified and ordered (with funds from another source). Almost a year expired to delievery of the device, and it was found to have serious design problems as well as manufacturing defects. After a great deal of back and forth with the supplier, this instrument may now be just about ready to test for ozone work.

Meanwhile, the old technique was pursued in our investigation of the Huggins system. When excitation spectra were taken of jet-cooled ozone (the 501 and 600 vibrational bands), the widths of the features narrowed by a factor of ~20 from the room-temperature spectra. This confirmed what we had suspected, that a large part of the room-temperature spectral width was due to rotational congestion. The new linewidth observation allowed a fresh estimate of the predissociative lifetime in the electronically excited state (~1 ps).

Further frequency narrowing of the excitation light actually permitted the partial resolution of rotational substructure in both vibrational bands, with individual rotational transitions estimated to be ~1.4 $cm^{-1}$ wide. This increased the estimate of dissociative lifetime to ~4 ps. Because of incomplete thermal equilibration of the jet beam and the intrinsic width of individual rotational lines, these lines could not be fully resolved. Instead, the partially resolved structure was modelled with an asymmetric rotor band contour program. This showed quite clearly that both the $1_0^5 3_0^1$ and $1_0^6$ vibrational transitions have the same rotational sturcture, which corresponds to an a-axis transition moment. If the equilibrium structure of the electronically excited state were of $C_{2v}$ geometry, spin statistics would make this impossible: the existing rotational states would be a different set for the $1^5 3^1$ level than for the $1^6$ level. Hence, we conclude that the electronically excited state has an equilibrium configuration only of $C_s$ geometry, i.e., the two O-O bonds are of unequal length. In this case, for a high "inversion" barrier, the $V_3$ quantum numbers would refer to single-well (left or right bond longer) levels. Each level, however, would be split into a closely spaced tunnelling doublet and one of the pair at any $V_3$ would support the correct rotational states for a-type transitions. Since ab initio calculations indicate a $C_s$ geometry for the $^1B_2$ excited state (and not for the $^1A_1$ state), we conclude that $^1B_2 \leftarrow \tilde{X}^1A_1$ is the correct electronic assignment for the

Huggins system. I.e., the Huggins band is actually just the wing of the Hartley band, the former corresponding to transitions into bound regions of the potential energy surface and the latter to transitions into a Franck-Condon region with no excited-state quasibound levels. The details of the rotational band-contour analysis permitted estimates of $^1B_2$ rotational constants: $A \approx 2.1 \pm .04$ cm$^{-1}$, $\bar{B} \approx 0.45.01$ cm$^{-1}$. Without data on isotopic variants these are not sufficient to establish a complete structure, but limits can be set on possible geometrics.

## Personnel Associated With Work Performed Under
## Contract F19628-80-K-0088

| Principal Investigator | Current Position |
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| James L. Kinsey | Professor of Chemistry, M.I.T. |
| **Graduate Students** | |
| Dan Imre | Asst. Professor, U. of Washington |
| Amitabha Sinha | Postdoctoral Fellow, NOAA, Boulder, CO. |
| **Postdoctoral Associates** | |
| James H. Goble | Talandic Research, Pasadena, CA |
| Michael O. Hale | Postdoctoral Associate, M.I.T. |

### Publications:

1. "Spectroscopic Characterization of Repulsive Potential Energy Surfaces: Fluorescence Spectrum of Ozone"
   D. G. Imre, J. L. Kinsey, R. W. Field, D. H. Katayama
   J. Phys. Chem. 86, 2564 (1982).

2. "Chemical Dynamics Studied by Emission Spectroscopy of Dissociating Molecules"
   D. Imre, J. L. Kinsey, A. Sinha and J. Krenos
   J. Phys. Chem. 88, 3956 (1984).

3. "Excitation Spectroscopy of Jet-Cooled Ozone: The Huggins System"
   A. Sinha, D. Imre, J. H. Goble and J. L. Kinsey
   to be sumbitted to Journal of Chemical Physics.

## Technical Presentations on Work Sponsored by Contract F19628-80-K-0088

Dam Imre: ACS Annual Meeting 1985
Gordon Conference on Molecular Electronic Spectrosocopy 1985
University of Washington 1984
Princeton University 1984
University of Texas 1984
University of Pittsburgh 1984
University of Oregon 1984

Amitabha Sinha: M.I.T. 1985
University of Colorado 1985
Air Force Geophysics Laboratory Ozone Meeting 1983

James L. Kinsey: University of Indiana - Gucker Memorial Lecture 1985
University of Illinois 1985
UCLA/USC/Caltech joint seminar 1985
University of Toronto 1985
University of Pennsylvania 1984
Harvard University 1984
Rutgers University 1984
XVI Informal Photochemistry Conference 1984
University of Rochester 1984
Dartmouth College 1984
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