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Richard A. Copeland Physics and Atmospheric Chemistry Group					
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<p>The main objective of this work is to investigate cryogenic solids containing ozone (O₃), oxygen molecules (O₂) and oxygen atoms (O) to evaluate their potential as components of an advanced propulsion system. SRI examined reactive processes involved in the decomposition of these solids with a vision toward creating a material that is less sensitive to unexpected explosion. We constructed an apparatus and proposed to study multilayer structures incorporating thin alternating layers of O₂ and O₃ to determine their potential for increasing the density of O₃ in O₂ while maintaining an acceptable margin of safety. The premature termination of the effort after less than one year of a proposed three-year effort caused a significant reduction in the proposed work. Techniques of isotopic substitution, thin-film matrix sandwich layers, and pump-probe picosecond spectroscopy were proposed for examination of the underlying processes in the O₃/O₂ solids. An important objective in the first year was construction of a new cryogenic apparatus to decrease the achievable temperature to 4K. This goal was achieved. This apparatus was required to investigate the introduction of oxygen atoms in a solid O₂ matrix. Finding direct spectroscopic evidence of large quantities of trapped oxygen atoms was an important new direction, given recent indirect measurements of trapped atoms by a research group at University of California, Irvine. From our one-year effort we concluded that oxygen atoms were not trapped in significant quantities in the O₂ matrix at 6 K because we could find no spectroscopic evidence for their later reaction. Concurrently with our investigation, the conclusions of the Irving work were modified, suggesting previously unexpected experimental issues contributed to their observation.</p>					
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ENERGETIC SPECIES IN CONDENSED OXYGEN/OZONE

Richard A. Copeland, Director
Physics and Atmospheric Chemistry Group
Molecular Physics Laboratory

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Prepared for:

Air Force Office of Scientific Research
110 Duncan Avenue, Suite B115
Bolling Air Force Base
Washington, DC 20332-8050

Attn: Michael R. Berman

SUMMARY

The main objective of this work is to investigate cryogenic solids containing ozone (O_3), oxygen molecules (O_2), and oxygen atoms (O) to evaluate their potential as components of an advanced propulsion system. SRI examined reactive processes involved in the decomposition of these solids with a vision toward creating a material that is less sensitive to unexpected explosion. We constructed an apparatus and proposed to study multilayer structures incorporating thin alternating layers of O_2 and O_3 to determine their potential for increasing the density of O_3 in O_2 while maintaining an acceptable margin of safety.

The premature termination of the effort after less than one year of a proposed three-year effort caused a significant reduction in the proposed work. Techniques of isotopic substitution, thin-film matrix sandwich layers, and pump-probe picosecond spectroscopy were proposed for examination of the underlying processes in the O_3/O_2 solids. An important objective in the first year was construction of a new cryogenic apparatus to decrease the achievable temperature to 4 K. This goal was achieved. This apparatus was required to investigate the introduction oxygen atoms in a solid O_2 matrix. Finding direct spectroscopic evidence of large quantities of trapped oxygen atoms was an important new direction, given recent indirect measurements of trapped atoms by a research group at University of California at Irvine.*

From our one-year effort we concluded that oxygen atoms were not trapped in significant quantities in the O_2 matrix at 6 K because we could find no spectroscopic evidence for their later reaction. Concurrently with our investigation, the conclusions of the Irving work were modified, suggesting previously unexpected experimental issues contributed to their observation.

DESCRIPTION OF EFFORT

The scientific results of this investigation are described in the two appendices attached to this report. This section summarizes our experimental approach and the modifications made to that approach due to the reduction of effort from a three-year project to a one-year project.

During the first nine months of this research effort, we focused on the design, construction, and vacuum testing of our new low temperature cryostat for trapping of oxygen atoms in low-temperature oxygen molecular matrices. This apparatus was going to be used extensively in years 2 and 3 of the proposed work to make multilayer structures of O_3 and O_2 . For these experiments, we designed a new vacuum apparatus, purchased a new cryostat with a ultimate temperature of 4 K, built a new cool finger with a quartz microbalance, and improved our gas mixing chamber so that we can measure the ozone pressure *in situ*.

In addition to the above construction, we obtained from SRI capital equipment funds approximately 60 K for the purchase of a higher resolution FTIR. This new piece of equipment

* Taborek, P., and J. E. Rutledge, in *Proceedings of the High Energy Density Matter (HEDM) Contractor's Conference Held 1-3 June 1997 in Chantilly VA*, Vol. PL-TR-97-3057, edited by P. G. Carrick and N. T. Williams (Air Force Materiel Command, 1998), pp. 151-154

that arrived at the end of September of 1998 was able to record spectra in the visible region in addition to its infrared capabilities. For applicability to this work, it is equipped with special optics and two infrared detectors so that we can rapidly switch from one cryostat to the other without additional alignment. Effort was expended to get this system interfaced to the newly constructed low temperature cryostat. Testing began on a quartz microbalance to monitor the thickness of low temperature matrices in the new system. By applying our established techniques for generating $O(^3P)$ and $O(^1D)$ atoms, we hoped to assess the storing of O atoms in 4 K solid oxygen.

Concurrently with the construction and testing during the first nine months, we continued our investigation on layered matrices of ozone and oxygen to investigate the thermal and photo-induced mobility of these species across layer boundaries and from regions of high ozone abundance to regions of low concentration. During this period, we focused on studying layers with large ozone concentrations (pure ozone to 10% mixtures with O_2) for comparison and contrast to our previous low concentration measurements. We examined the α to β phase transition in solid O_2 in more detail and performed kinetic measurements on the dimerization of ozone in both phases and near the phase transition. A hysteresis in the phase transition was examined and found to be sensitive to the surrounding environment in the low temperature matrix.

When informed by the contract monitor that the funding for years 2 and 3 was at risk due to program cuts, we changed our experimental approach significantly to address the important question of storage of O atoms in solid O_2 at 4-10 K. Appendix 1 describes the results of that refocused effort. We halted construction of the new system and modified our old system to get some experimental results on this topic before the termination. These modifications of approach, undertaken under aggressive time and funding constraints, proved very successful. Our conclusion that oxygen atoms are not stored in O_2 matrices in large concentrations has been supported by later experiments.

Because of lack of funds, publication outside of AFOSR reports has been limited. The following summarizes the other experimental results found in this investigation during the construction of the new apparatus.

We determined the aggregation of ozone-doped O_2 matrices to be governed and limited to dimerization in the β phase of oxygen ($T > 24$ K). This property is important for understanding the structure and stability of ozone/oxygen mixtures as it relates to the well-known shock sensitivity of solid ozone. Photochemical studies on these samples as a simulation of spontaneous ignition yielded no shock sensitivity despite our qualitative results, indicating a large mobility of O atoms in the solid. The specifics of these studies are describe in Appendix 2.

PERSONNEL SUPPORTED

The following researchers were partially supported by or worked on this project during the contract:

Dr. Richard A. Copeland, Principal Investigator

Dr. Jean Lacoursière, postdoctoral assistant

Dr. Christian Bressler, visiting scientist

Dr. Robert Robertson, visiting scientist

Emmely Templeton, National Science Foundation Research Experiences for Undergraduate Students, summer research assistant

Drs. Lacoursière and Bressler have both found permanent positions in industry and academics, respectively. Dr. Lacoursière is currently employed with TTI Medical of San Ramon, California, as an optical design engineer for medical equipment. The experience he gained in designing the new cryogenic system and working with FTIR, lasers, and light detectors was a key factor in his obtaining this industrial position. Dr. Bressler is now working at the University of Lausanne in ultrafast photochemical reactions on complex systems with combined laser and synchrotron radiation. On this AFOSR project, he introduced a clear experimental strategy to extract important information on otherwise very complicated processes occurring in the HEDM material. The applied problem solving served him well in his future efforts.

Dr. Robert Robertson is a visiting scientist from a local semiconductor equipment manufacturing company (Applied Komatsu Technology, a spin-off of Applied Materials Corporation), who is spending a sabbatical in the laboratories of Dr. Copeland. He hopes to learn new methods and approaches during his tenure at SRI International and then transition those new ideas to the semiconductor industry. His participation in the research has been extremely useful, bringing an industrial perspective to the work and providing inspiration for ideas on where our new technology could be applied to new issues.

Emmely Templeton is the third Research Experiences for Undergraduate Student program member that has worked on this and the previous AFOSR projects. She attended Portland State University. Her participation is funded by NSF and gives undergraduate students an opportunity to sample contract research early in their careers. Previous REU students, Brian Schwartz and Stephanie Sublett, have continued in science and related fields. Mr. Schwartz acquired his B.S. in physics in 1997 by submitting his SRI work on the HEDM project as his senior thesis at Swathmore College. He worked for New Focus of Santa Clara, California, a company that develops and distributes optical components and mounts. New Focus was initially interested in his experience because of his practical experience with our FTIR equipment. Recently, he left New Focus to attend graduate school in optics. Ms. Sublett is attending the University of Rochester in the fall and is enrolled in the Physics and Astronomy Program graduate program.

INTERACTIONS/TRANSITIONS

The results of the AFOSR supported research were described at the following meetings, conferences and seminars.

1. Richard Copeland attended the High Energy Density Matter Contractor's Review held in Cocoa Beach, Florida, in June, 1999. During the HEDM meeting, he presented a poster on the work described in Appendix 1.
2. Richard Copeland attended both the High Energy Density Matter and the Molecular Dynamics Contractor's Review held in Monterey, California, May 17-22, 1998. During the HEDM meeting, he gave an oral presentation entitled "Stability and Mobility of O Atoms and Ozone in a Oxygen

Matrix." At the Molecular Dynamics meeting, he presented a poster entitled "Production, Detection, and Collisional Energy Transfer of O₂ in the ⁵Π_g State."

3. Richard Copeland, as part of the NSF Research Experiences for Undergraduate Students at SRI, presented a review of SRI's cryogenic research to all the students.
4. Christian Bressler presented a special seminar entitled "Ozone in Solid Oxygen: Temperature Effects, Photochemistry and O-Atom Mobility" at the Institut of Experimental Physics at the University of Lausanne in November of 1997.

In addition to the meetings listed above Dr. Copeland also attended the 1997 Fall Meeting of the American Geophysical Union, where he met with several Air Force scientists performing research on atmospheric light emission and the NASA Laboratory Space Science Workshop, where interaction with NASA laboratory researchers was highlighted

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES

No inventions were discovered and no patent disclosures were filled.

HONORS/AWARDS

None

CONCLUSIONS

Our study of low temperature solid O₃/O₂ mixtures yielded very interesting results on O atom and O₃ mobility in solid oxygen over the temperature region of 6 to 40 K. SRI researchers made the best of a difficult situation of anticipating a three-year program and having the funding cut down to one year during the construction phase of a new apparatus. Preliminary experiments were designed and conclusions were drawn about the ability to store significant quantities of O atoms in solid molecular O₂. With the redesigned apparatus we found no spectroscopic evidence that significant amount of O atoms could be stored in solid O₂ at 6 K using both microwave discharge and ultraviolet laser photodissociation to generate the O atoms.

APPENDIX 1

Generation of Energetic Species in Solid Oxygen

Richard A. Copeland and Robert Robertson
Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

The purpose of the HEDM program is to research and develop high energy density propellants with greater specific impulse, and one strategy has been to study energetic species in cryogenic solids. At SRI International we have focused on energetic species that could be incorporated in solid oxygen[1-3] with the approach of doing basic investigations that will be important for solving practical problems. In the several years of this effort we have developed an expertise in macroscopic crystals, thin film matrices and a variety of the energetic species (O atoms, ozone and O_x compounds) that can exist in these solids. Through the investigation of spectroscopy, photophysics and reactivity we have gained new understanding of solid O_2 : defect annealing by temperature and light, phase transition monitoring, phase transition hysteresis, and photodecomposition by nanosecond and picosecond irradiation. For the most discussed energetic species, ozone, we have gained many new insights: stable and unstable monomer and dimer states, photoactivity of these states, and dynamics of multilayers through isotopic substitution. Through our approach of basic investigation we identified an unstable state of the monomer that had previously been incorrectly identified by Schriver-Mazzuoli et al [4] as a trapped O atom, the $O_3^{\cdot\cdot}O$ compound.

The recent series of experiments were performed to determine if O atoms can be trapped in solid oxygen at low temperatures. Trapped atoms would be the ideal energetic species since there is no energy penalty to convert them to their most reactive state. The problem of course is preventing recombination or reaction during storage and delivery to the combustion zone. The possibility of trapping O atoms was raised again by Taborek and Rutledge [5]. In our experiments we used two methods to generate the O atoms in the films: UV phototgeneration from O_2 in the solid oxygen film, and deposition of the products of a microwave discharge in O_2 gas. The solid oxygen films were formed on a substrate that was held at 6 K to reduce the O-atom thermal energy which could increase the rate of reaction with O_2 to form O_3 . Because O atoms cannot be directly detected with our Fourier transform infrared (FTIR) spectrometer we inferred the presence by the formation of O_3 , which would be formed as the sample was warmed to 15 K.

EXPERIMENT

For this series of experiments we significantly improved the capabilities of the apparatus with the installation of new equipment: lowering the sample temperature (from 15 to 6 K), and improving FTIR detection sensitivity and resolution (from 0.5 to 0.125 cm^{-1} .) The film samples were deposited on a gold-coated copper substrate (1" diameter) from room temperature gases. The substrate was attached to a new liquid He cryostat which was mounted on the top of the vacuum chamber. The He cryostat could be raised and lowered to put it in contact with a closed-cycle He refrigerated finger (minimum temperature of 15K) which was mounted from the bottom of the vacuum system. The He refrigerated finger was utilized to conserve liquid He: by doing initial cool down and by cooling a heat shield to reduce radiative heating of the sample. The

sample temperature was controlled by adjusting the temperature of the He refrigerated finger using a resistive heater. The substrate temperature was measured by a Si diode attached to the back of the gold-coated copper substrate. A new high resolution FTIR (Nicolet Co., model MAGNA-IR 760) was put into service for this series of experiments. The IR beam enters the vacuum system through an IR window, reflects off the substrate, and then passes out of the vacuum through another IR window to the MCT detector. The beam was focused with gold coated front-side mirrors to provide a ~ 1 cm diameter spot on the substrate. The improved resolution and beam focusing allowed us to resolve spectroscopic features not seen before.

To test the new apparatus we performed a simple experiment, O_3 seeded in O_2 , that has been performed in the past. In this test we measured the spectra of a sample (approx. 1% O_3 concentration.) at different temperatures: as deposited at 6 K, annealed to 30 K, and re-cooled to 6 K. The absorbance in the ν_3 region of ozone is shown in Fig. 1. The absorbance is defined as $\log(1/TR)$ where TR is the fractional transmission. This is the preferred parameter for quantitative analysis because it is proportional to the product of density, absorption coefficient, and path length. During this annealing cycle the appearance of the sample changed from glassy to hazy at 26 K and remained hazy when re-cooled to 6 K. The annealing changes the film from crystalline to amorphous and removes defects in O_2 matrix. The spectra had the same features that were discussed in previous reports: the stable monomer peak (M at 1038 cm^{-1}), the unstable monomer peak (M' at 1031 cm^{-1}) which disappears upon heating, and the dimer peaks (D at 1040 and 1042 cm^{-1}) which are formed upon heating and persist when the sample is re-cooled. This same sample was further examined while the temperature was gradually increased. The position of the primary monomer peak was monitored to determine the temperature of the transition from α - O_2 to β - O_2 . Near the transition we observe two distinct peaks indicating that both phases exist simultaneously. We had not observed this in previous studies using a lower resolution FTIR. The α/β transition was at 24 ± 1 K indicating good calibration of the Si diode sensor (expected value of 23.9 K.)

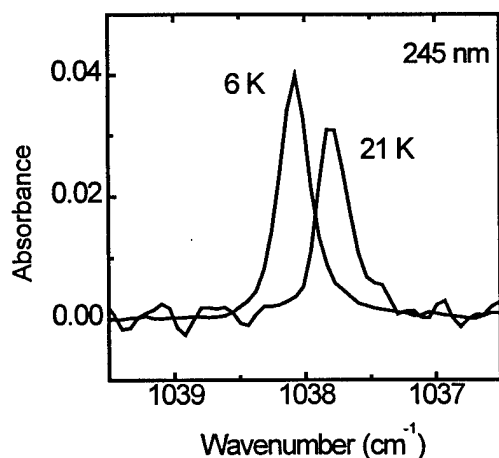


Figure 1. FTIR spectra of a sample irradiated with 245 nm light at 6 K and subsequently heated.

UV PHOTOGENERATION

In the UV photogeneration experiment we used the frequency doubled output of an excimer-pumped dye laser to irradiate the solid oxygen samples at wavelengths from 230 to 250 nm. The UV beam entered the vacuum system through a quartz window and was focused to provide a ~ 1 cm diameter spot on the sample coincident with the IR beam. In the first test we irradiated an O_2 film with 230 nm light for comparison to previous experiments. The spectrum taken with the new FTIR had many absorption features that were not resolved in the previous tests.

In a second set of experiments we used irradiation wavelengths that were only

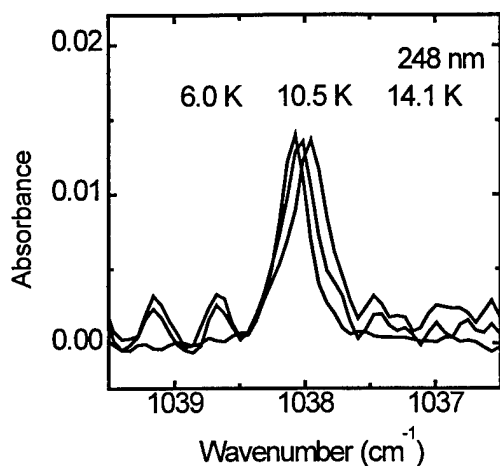


Figure 2. FTIR spectra of a sample irradiated with 248 nm light at 6 K and subsequently heated

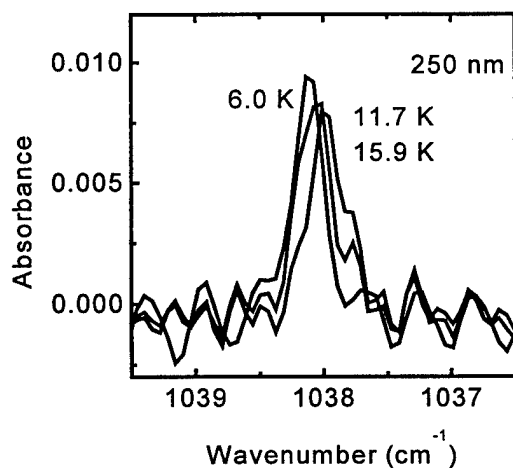


Figure 3. FTIR spectra of a sample irradiated with 250 nm light at 6 K and subsequently heated.

determine precisely because the thicknesses were not known. However based on our experience with seeded samples we expect that the sensitivity was better than 0.1 %. At higher temperatures (>25 K) we observed the disappearance of the M' peak and appearance of the dimer peak.

slightly below the threshold for dissociation of O₂, so the absorption cross section was small and long irradiation times were required to generate sufficient dissociation. The purpose of operating near the threshold was to limit the O-atom kinetic energy which otherwise might be sufficient to overcome any barrier to the reaction with O₂ to form O₃. During irradiation O₃ was observed to be formed, so some or all of the O atoms reacted immediately to form O₃. Any trapped O atoms would be expected to form additional O₃ as the temperature was raised.

In Fig. 1, 2, and 3 we show ν_3 region of the spectrum of O₃ after irradiation with progressively longer wavelengths. The samples were deposited at 30 K from pure O₂ and then cooled to 6 K. The film thicknesses and irradiation time were increased for the longer wavelength experiments. For 245 nm light we irradiated for 60 minutes at an average pulse energy of 420 μ J per pulse (30 Hz, total dose = 45.3 J). For 248 nm light we irradiated a 3 times thicker sample for 120 minutes at an average pulse energy of 260 μ J per pulse (30 Hz, total dose = 55.6 J). For 250 nm we irradiated a 6 times thicker film for 180 minutes with an average pulse energy of 160 μ J (30 Hz, total dose = 51.8 J).

For all three cases we only observe M and M' features after irradiation. This is in contrast to shorter wavelength irradiation which produces many dimer peaks. Upon heating to ~15 K there is no appreciable production of O₃ from O atoms trapped at 6 K for any of the three cases. The sensitivity in concentration units is difficult to

MICROWAVE DISCHARGE

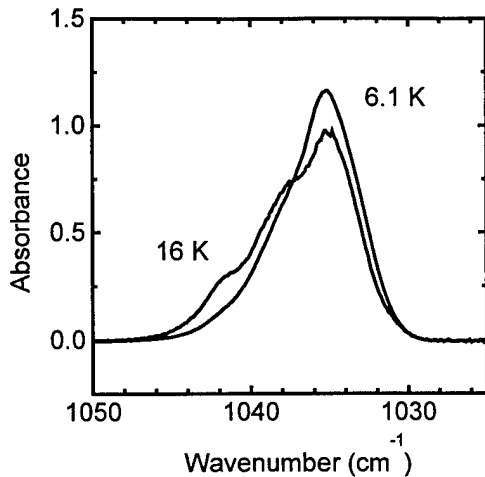


Figure 4. Ozone spectrum of a microwave discharge sample deposited at 6.1 K and subsequently heated to 16 K. The discharge conditions were 4 sccm O₂, 200 mTorr, and 40 W.

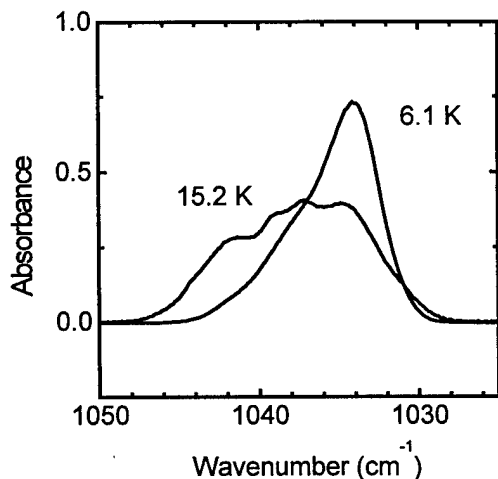


Figure 5. Ozone spectrum of a microwave discharge sample deposited at 6.1 K and subsequently heated to 15.2 K. The discharge conditions were 7 sccm of 10% O₂ in He, 400 mTorr, and 40 W.

In the second set of experiments we deposited film samples at 6 K from the products of a microwave discharge in O₂: the stable species O₂ and O₃, and to a lesser extent atoms, ions and excited species. The discharge was in a 10" long, 1/2" diameter pyrex tube. For the first two runs the end of the tube was constricted with a 1/4" tube to reduce conductance. For the last experiment the 1/4" tube was removed reduce the residence time of the reaction products in the discharge tube. A clamshell type microwave applicator was placed in the middle of the tube.

In Fig. 4, 5, and 6 we show the temperature dependence of the FTIR spectra at the ν_3 mode of O₃ for three deposition conditions. The conditions for the experiment in Fig. 4 were 4 sccm O₂, 200 mTorr, and 40 W. The conditions for the experiment in Fig. 5 were 7 sccm of 10% O₂ in He, 400 mTorr, and 40 W. This high pressure was required to sustain the discharge. The conditions for the experiment in Fig. 6 were 6 sccm of O₂, 80 mTorr, and 30 W. In this experiment the restriction at the end of the tube was removed. The deposition time for all three cases was approximately 5 minutes.

For all three cases, we observed a shift in spectra but no appreciable increase in the total peak area as the temperature was raised. This indicates that there was no significant production of new O₃ from O atoms that were trapped at 6 K. The ν_3 band of O₃ was the strongest absorption feature in these spectra. Many other absorption features were present but were much weaker. We identified many features as being due to the other absorption bands of O₃ and due to CO, CO₂ and OH.

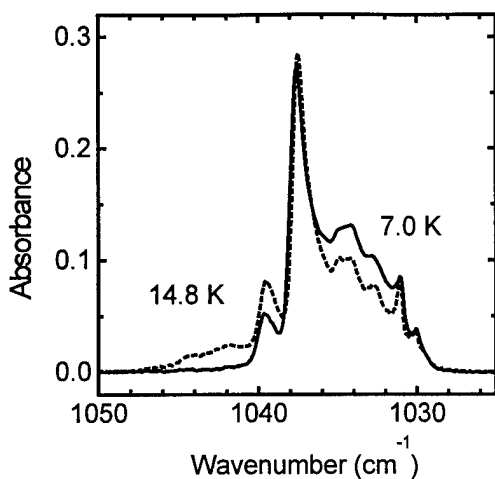


Figure 6. Ozone spectrum of a microwave discharge sample deposited at 7 K and subsequently heated to 14.8 K. The discharge conditions were 6 sccm O₂, 80 mTorr, and 30 W.

sensitivity for the product O₃. We conclude either our discharge and deposition conditions (they used rf discharge) were significantly different or the heat released in their experiment was due to a different process.

The new apparatus did perform well and did show some interesting new absorption features. The new apparatus will make new basic investigations possible.

This work is supported by the AFOSR-HEDM program.

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CONCLUSION

The two series of experiments failed to demonstrate the trapping of O atoms in O₂ matrices at temperatures down to 6 K. Our results cannot confirm the claim by Taborek and Rutledge [5] that O atoms can be trapped in matrices prepared by rf discharges in O₂ at this temperature. Their hypothesis was based on calorimetric studies of samples in which they observed heat release upon warming. In their experiment they were not able directly observe the species in the O₂ matrix. Using the observed excess energy they estimated a lower limit for the amount of O atoms as 0.64% based on assumptions of the reaction (5 eV for O+O) and energy accommodation coefficient (100%.) The concentration would be higher for other assumptions including the more likely reaction O+O₂. Even the lower limit is well above our measurement

APPENDIX 2

STABILITY AND MOBILITY OF O ATOMS AND OZONE IN AN OXYGEN MATRIX

Richard A. Copeland, Christian G. Bressler, Stephanie Sublett, and Jean Lacoursière
Molecular Physics Laboratory, SRI International, Menlo Park, California 94025

INTRODUCTION

A goal of the High Energy Density Matter (HEDM) Program is to develop propulsion systems with performance exceeding that of current liquid hydrogen/liquid oxygen motors. Storage of energetic species in cryogenic solids is one means to achieve that goal. The increased density of solid oxygen or hydrogen gives improvement in the specific impulse, the key figure of merit, but the increased complexity of the cryogenic solid motor system might outweigh the modest fuel density increases. Crucial to a significant advance is incorporation of an energetic species in high concentrations into the solid hosts to dramatically enhance performance. This energetic-species generation and storage task is a difficult experimental challenge.

Our laboratory effort is based on the following premises:

- solid oxygen will be a key component of future systems
- an energetic species must be added to the solid oxygen
- the concentration of the additive will exceed 5% for improved performance
- extremely large quantities of the propellant will be required
- the envisioned solid energized propellant will be imperfect, i.e., contain defects, flaws, and complexity due to both growth conditions and subsequent processing (i.e. experiments on single crystals are important but may not be directly relevant).

The majority of our experiments are performed in solid oxygen prepared by a variety of experimental techniques, allowing studies on samples with differing amounts of defects, crystal sizes, and seeded energetic materials. Our prototype energetic additive is ozone; it can be produced and handled in the laboratory, seeded in large concentrations, and can be monitored via Fourier-transform infrared (FTIR) spectroscopy. For future fuel production, ozone can be manufactured in ton quantities with existing technology -- a distinct advantage. Handling large quantities of ozone is currently problematic because of its shock sensitivity and its proclivity for unanticipated explosion. Understanding the physical processes that occur in ozone/oxygen mixtures will provide important insight into energetic-species-seeded cryogenic propellants in general and specifically address important issues in the shock sensitivity of ozone-containing materials.

EXPERIMENTAL APPROACH

In order to study ozone/oxygen solids, we must be able to look into the solid with a non-intrusive diagnostic that provides detailed information on the stimulated processes occurring in the sample. We use FTIR spectroscopy for the majority of our investigations since our previous work has shown that the IR source does not alter the properties of the cryogenic samples. We must also prepare the samples with well-characterized and reproducible properties. This goal is achieved using *in situ* production and processing with wavelength-tunable laser light as well as with conventional cryogenic preparation techniques employing mixtures of ozone and oxygen, sometimes containing isotopic $^{18}\text{O}_2$ as a photochemical marker. Ozone infrared absorptions in solid O_2 change with the method of sample preparation and ozone concentration. At low concentrations we have already extracted detailed information about the kinetic processes occurring within the matrix. At higher concentrations the absorptions broaden and become more complex. These changes indicate that new experimental approaches must be used in future experiments.

Details of the experimental approach are described elsewhere.¹⁻³ Briefly, all experiments are performed on thin films generated from room temperature gas phase deposition of oxygen/ozone mixtures deposited on a gold-coated copper substrate. Sample temperature is maintained between 15 and 50 K with a closed-cycle helium refrigerator and heater system. An apparatus using a liquid helium cryostat is under construction and with this system we will obtain temperatures down to 4 K. Picosecond and nanosecond lasers tunable in the visible and ultraviolet are used for the studies involving the interaction of the sample with light. The absorption spectrum of the samples is recorded using an FTIR spectrometer in the 500 - 4000 cm^{-1} range with a resolution of 0.5 cm^{-1} . The entire spectral region is acquired, but in this brief report we will focus on the ν_3 region of the ozone absorption between 1020 and 1055 cm^{-1} . The absorptions in this region are sensitive to the site occupied by the ozone in the oxygen matrix.

REQUIRED BACKGROUND INFORMATION

In order to discuss the specific experiments described below, we summarize the properties of solid O_2 and the ν_3 absorption of ozone in the O_2 matrix. At atmospheric pressure, O_2 exists in three phases, α , β , and γ , depending on the temperature. Below ~ 24 K oxygen is in the α phase, between 24 and 44 K it is in the β phase, and between 44 K and the melting point at 55 K it is in the γ phase. Given the low pressures in the ultra high vacuum reaction chamber we can only investigate the α and β phases at temperatures less than 29 K. For most of the potential applications as a propellant, those phases and this temperature range are the most relevant. For trapping and isolating energetic species the lower the temperature the better, and some of the experiments described below illustrate this point quantitatively.

In previous reports, we showed that irradiation of cryogenic oxygen matrices with ultraviolet light results in the production of ozone monomers and dimers locked in specific sites with unique orientations.¹⁻³ The spectroscopy, photophysics, and stability of these ozone species

are studied using FTIR spectroscopy. With FTIR spectroscopy and the unique spectroscopic signatures of specific species and sites we gain a window into the processes occurring in the matrix, and we can examine the behavior of oxygen species seeded in the host. Following many investigations we have identified absorption features as M or D depending on if the absorption is due to an ozone monomer (M) or dimer (D) in the matrix. Two monomer sites have been identified and eight dimer sites. The monomer sites show up in both photon-produced and seeded ozone at the same infrared frequencies but interestingly different dimers are produced generating different absorptions for each preparation method. Details of this difference are given in previous reports.¹⁻³ For what follows in this report, remember that M sites are caused by ozone monomers and D sites are caused by ozone dimers.

TRAPPING ABILITIES OF SOLID OXYGEN

The ability of solid oxygen to trap energetic species is important for understanding HEDM oxygen systems. Our experiments show that in the α phase of oxygen ($T < 24$ K), the prepared ozone/oxygen sample does not change with time, but within the β phase, isolated ozone molecules can migrate through the solid and find another ozone to form a dimer.

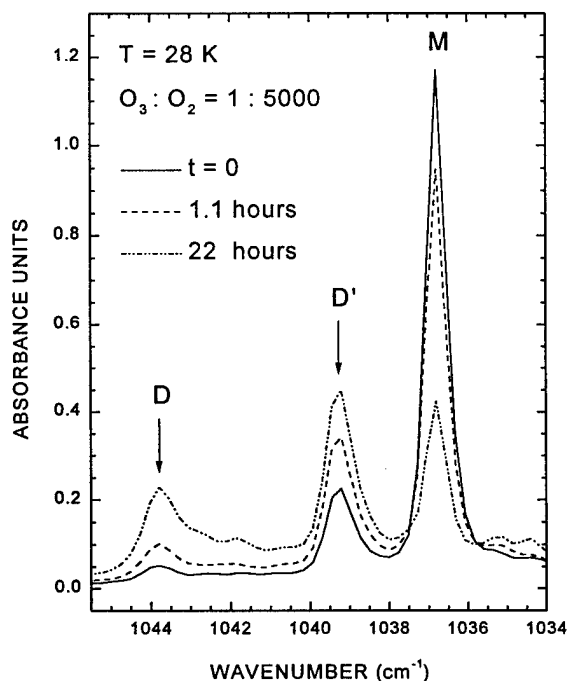


Figure 1

through the sample. When the sample is cooled all features in the spectrum no longer change with time. Through irradiation with ultraviolet (Hartley-continuum) or visible (Chappuis bands) light, the M absorption can be increased due to photodissociation of the dimers.

Figure 2 shows the quantitative results of experiments like those shown in Figure 1 for the temperature dependence of the ozone monomer removal rate in a diluted sample ($O_3 : O_2 = 1 : 5000$ of one part ozone to five thousand parts O_2). Below the phase transition only

the feature attributed to the monomer of ozone, labeled M, decreases as a function of time at 28 K while the features due to dimers, D and D', increase. Measurements have been made at several temperatures above the phase transition and upper limits extracted for measurements below the phase transition. Careful examination of the dimer growth curves show that the D' feature grows in more rapidly than the D feature. The rates exhibit the kinetics appropriate to the movement of ozone through the lattice. We believe ozone movement must be associated with the transport of an O_2 hole and the nearby ozone

upper limits are extracted for the removal of the absorption due to dimerization. Once the temperature of the α - β phase transition is exceeded, measurable rate constants are obtained. As can be seen in Figure 2 the rates also increase as the temperature is increased in the β phase. In other measurements we have changed the concentration of the ozone in the solid oxygen and have also seen the rate constant increase with temperature in the β phase. A complete kinetic analysis will be published in a future manuscript.

The observed thermal mobility of ozone monomers in the β -phase of solid oxygen may foreshadow some difficulties for storing this mixed propellant at such elevated temperatures. In a simple scheme, liquid hydrogen (< 21 K) could serve as the coolant for the ozone/oxygen solid. Temperatures near the phase transition would be anticipated in a motor cooled in this manner.

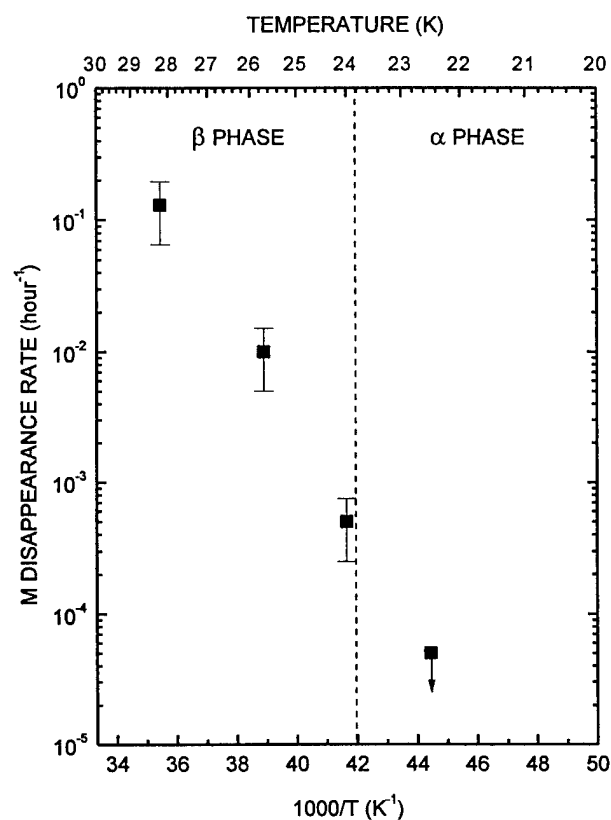


Figure 2

This danger of ozone aggregation can be readily excluded from our detailed investigations of the ozone mobility in the β -phase. Our results not only show the remarkable monomer migration, but also the nearly complete immobility of the generated ozone dimers. If these species were also mobile, then we would observe a growth of the extremely broad aggregate absorption band, which overlaps the entire region displayed in Fig. 1. Ozone dimers are apparently stronger bound to each other via dipole-dipole interaction. A migration of these ozone pairs is extremely unlikely due to the enhanced size of these species with respect to the oxygen lattice. Hole-assisted migration, as described for the monomer movement, is too unlikely, since one hole is too small to assist a correlated dimer jump. Therefore our results are already interesting for this practical avenue of fuel-storage, but still more research is required to quantify our measured immobility of ozone dimers and aggregates. The size of the species clearly matters in the movement through the solid oxygen.

We have started to perform quantitative studies on the behavior of ozone species in the solid host due to photon irradiation. Such studies are required to assess the mobility of oxygen atoms, which may be a component of future propellants. Currently, our studies show that irradiation with visible light (532 nm), thus generating $O(^3P)$ atoms and vibrationally excited O_2

ground-state molecules, generates more O₃ with irradiation time. This indicates a catalytic process involving the solid oxygen host, since the low intensity green light can not dissociate a host oxygen molecule. In addition we find that photogenerated O atoms move over significant distances in the sample. These interesting results require further study in order to elucidate the elementary chemical behavior of ozone-enriched solid oxygen.

FUTURE EXPERIMENTS

Over the past three years, our project has developed a variety of new experimental methods to generate, characterize and process solid oxygen and mixtures of oxygen with ozone. Since high concentrations of energetic species is a goal of the HEDM program much of the future work will concern ozone concentrations above 10% and some of the work will be on pure ozone.

The commissioning of a novel setup dedicated to this advanced fuels research contains a liquid flow He cryostat. The apparatus will thus be capable of cooling our samples down to 4 K. At such low temperatures it was reported that ground state O atoms are trapped in the oxygen solid [4]. It was also emphasized, that 15 K sample temperature is already above the barrier for thermally induced ozone generation. With our established spectroscopic tools in the UV-IR spectral range we are capable of delivering additional relevant information to this possible breakthrough in developing a next generation's rocket propellant.

We will thus continue our photochemical work on cold 4 K samples, and relate their properties to more convenient temperatures above the boiling point of liquid hydrogen. For the high concentrations envisioned in our future work isotopic substitution and layer structures of different isotopic composition will play an important role. Both strategies allow determination of elementary dynamic and static properties of the future propellant. Isotopic substitution facilitates the observation of (initially) low concentrated products, while layer structures aid in determining precise and reliable pathlengths for both thermal induced and photoinduced mobility and chemical reactions.

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