ATMOSPHERIC OXYGEN PHOTOABSORPTION

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CONTENTS

SUMMARY ................................................................. 1

ACCOMPLISHMENTS .................................................. 2

PUBLICATIONS RESULTING FROM THIS GRANT .................... 6

REFERENCES .................................................................. 7

APPENDICES .................................................................. 9
SUMMARY

The work conducted on this grant was devoted to various aspects of the photophysics and photochemistry of the oxygen molecule. Predissociation linewidths were measured for several vibrational levels in the $O_2(B^3\Sigma_u^+)$ state, providing good agreement with other groups working on this important problem. Extensive measurements were made on the loss kinetics of vibrationally excited oxygen, where levels between $v = 5$ and $v = 22$ were investigated. Cavity ring-down spectroscopy was used to measure oscillator strengths in the oxygen Herzberg bands. The great sensitivity of this technique made it possible to extend the known absorption bands to the dissociation limit as well as providing many new absorption lines that seem to be associated with new $O_2$ transitions. The literature concerning the Herzberg band strengths was evaluated in light of our new measurements, and we made recommendations for the appropriate Herzberg continuum cross sections to be used in stratospheric chemistry. The transition probabilities for all three Herzberg band systems were reevaluated, and we are recommending a new set of values.
ACCOMPLISHMENTS

The general theme of the research program was the chemical and physical properties of O₂ as they relate to atmospheric processes. The number of issues is diverse, and several topics were clarified for which uncertainties have existed for many years. This section summarizes what has been accomplished, and the Appendix includes the abstracts of the five published papers and the two papers in preparation that resulted from these studies.

The transparency of the mesosphere and upper stratosphere to solar radiation is a sensitive function of the spectroscopic details of O₂ absorption, since absorption in the $B^3Σ_u^+ - X^3Σ_g^+$ Schumann-Runge bands is the filter through which solar radiation must pass. Because the linewidths are quite variable and depend on vibrational level, rotational level, and spin multiplet, an accurate knowledge of the widths as a function of these parameters is essential.

In our initial paper, in which only the $v = 0$ and $v = 2$ levels of the $B^3Σ_u^+$ state were investigated (the $v = 0$ level for the first time), we demonstrated the effectiveness of the technique of photodissociating ozone to produce vibrationally excited ground state levels, which then become stepping stones for generating an array of vibrational levels in the upper state. The new data significantly revised the state of knowledge up to that time.

These studies have been extended to the $v = 1$ level and to levels above $v = 12$. Levels in the $v = 3-12$ range tend to be uninteresting to us, because their widths are so great that they are easily measured and not controversial. The new measurements extend up to $v = 16$, coming very close to the dissociation limit of the $B^3Σ_u^+$ state. We have been collaborating with other groups worldwide: Brenton Lewis' group at the Australian National University, Yoshino’s group at Harvard-Smithsonian, and Ginter at the University of Maryland. These investigators use techniques distinctly different from ours, yet agreement on the linewidths is reaching a very satisfactory state. We consider this research very successful.
The other side of the coin, using ozone photodissociation to prepare the vibrationally excited O₂ levels, provides us with an enormous O₂(vib) distribution: \( \nu = 0-22 \), when using 248-nm laser radiation for dissociation. With this distribution, we are then able to investigate the kinetic behavior of these energetic molecules, using O₂, N₂, O₃, CO₂, and He as quenchers.⁴ An early premise of ours,⁵ that solar radiation could play a role in photodissociating O₂(vib), was shown to be incorrect, because quenching by O₂ and N₂ in the atmosphere is too fast, by a factor of at least ten, to make the process interesting.

We showed that the quenching rates by O₂ exhibited a minimum near \( \nu = 19 \), where \( V \rightarrow T \) quenching takes over from \( V \rightarrow V \). An important observation is that there is a resonance between the fundamental N₂ vibrational quantum and two O₂ quanta near \( \nu = 19 \). Thus, the N₂ quenching rate coefficients show a peak in this region and dominate the O₂ rate coefficients. The rate coefficients we determined have been the subject of several modeling and theoretical studies.⁶⁻⁸ Together with the recent work by Wodtke and colleagues,⁹⁻¹¹ these studies are the first to measure kinetics other than for the lowest levels of O₂(vib).

These latter researchers found an interesting effect that sets in at O₂(\( \nu = 26 \)) in the quenching of O₂(\( \nu \)) by O₂,⁹ in that the rate coefficient increases markedly. In several publications, they claimed that this observation indicates a new stratospheric ozone source.⁹⁻¹² Because they have not demonstrated that either ozone or oxygen atoms appear, we have been critical of their conclusions. As a consequence, when they submitted a major article to Science,¹² I was asked to write a Perspective, in which I described the present state of understanding of oxygen photochemistry and put their work in context.¹³ In a recent publication, they seem to be retreating from the idea that the reaction produces ozone.¹⁴

One of the critical aspects of stratospheric photochemistry is to have accurate knowledge of the photoabsorption cross sections for the primary process making ozone, the photodissociation of oxygen in the Herzberg continuum, at 190-242 nm. One of the best demonstrations of the correctness of a measurement is that the photoabsorption cross section is continuous between the
continuum, below 242 nm, and the integrated absorption cross sections for the three bound-bound Herzberg systems above 242 nm.\textsuperscript{15}

In collaboration with G. Meijer's group at the University of Nijmegen, we made new determinations of the absorption oscillator strengths for the three Herzberg systems, using the newly developed technique of cavity ring-down (CRD) spectroscopy. The sensitivity of this system for absorption measurements is extremely high, and we measured absorption to the five uppermost \( \text{O}_2(A^3\Sigma_u^+ ) \) levels. The particular arrangement suffered from a laser linewidth that was too large, and as a result, the oscillator strengths were about 20\% too small. However, we evaluated all existing data and performed theoretical calculations,\textsuperscript{16} ultimately concluding that the current Herzberg continuum cross sections of Yoshino et al.\textsuperscript{17} and an older set of Herzberg I cross sections by Hasson et al.\textsuperscript{18} are the most compatible and best represent the true state of affairs. A new paper by Amoruso et al.\textsuperscript{19} has muddied the waters by reporting continuum cross section values lower than those of Yoshino et al.,\textsuperscript{17} but we conclude that this work is erroneous because it does not meet the test of blending with what we consider the best Herzberg I band measurements.

After these CRD studies, we decided to use the system sensitivity to search for additional Herzberg bands, because there is a substantial gap between the last known levels in the upper state and the \( \text{O}_2 \) dissociation limit. In this endeavor we were successful, in that we found one new \( A^3\Sigma_u^+ \) state level, two for the \( A^3\Delta_u \) state, and two for the \( c^1\Sigma_u^- \) state.\textsuperscript{20} The new \( A \) state level, \( \nu = 12 \), is bound by only 7 cm\(^{-1}\), yet is in precisely the predicted position.

A remarkable consequence of this study is that, after assigning many absorption lines to these five new bands, we still have some 100 lines remaining, which appear to also belong to \( \text{O}_2 \). There are weakly bound states that have long been proposed as potentially important in the atmosphere,\textsuperscript{21-23} and it seems that the present measurements represent the first indication of their presence. More CRD work is planned, using isotopes to explore the spectroscopy and identify the states.
With all our work on quantification of the Herzberg state transitions, we are now able to revise the currently accepted values of oscillator strengths for the three systems, those of Bates's.\textsuperscript{24} It has been evident to us, from comparison of relative band strengths in experimental data, that Bates' calculations were incorrect. We have a paper in preparation in which significant changes have been made in the absolute band strengths and radiative lifetimes, which we believe represents the best available values.\textsuperscript{25}
PUBLICATIONS RESULTING FROM THIS GRANT


H. Park and T. G. Slanger, "\( \text{O}_2(X, v = 8-22) \) 300 K Quenching Rate Coefficients for \( \text{O}_2 \) and \( \text{N}_2 \), and \( \text{O}_2(X) \) Vibrational Distribution from 248 nm \( \text{O}_3 \) Photodissociation," J. Chem. Phys. 100, 287 (1994).


D. L. Huestis and T. G. Slanger, "Revised Transition Probabilities for the \( A^3\Sigma_u^+ -X^3\Sigma_g^- \), \( A^3\Delta_u -X^3\Sigma_g^- \), and \( c^1\Sigma_u^- -X^3\Sigma_g^- \) Herzberg Systems of \( \text{O}_2 \)," J. Geophys. Res. (in preparation).
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APPENDICES


A-2 H. Park and T. G. Slanger, “\( \text{O}_2(X, \nu = 8-22) \) Quenching Rate Coefficients for \( \text{O}_2 \) and \( \text{N}_2 \), and \( \text{O}_2(X) \) Vibrational Distribution from 248 nm \( \text{O}_3 \) Photodissociation,” J. Chem. Phys. 100, 287 (1994).


Predissociation linewidths in $\text{O}_2 B^3\Sigma_u^-$ ($v=0,2$)

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Using laser-induced fluorescence techniques applied to Schumann–Runge absorption transitions from vibrationally excited $\text{O}_2 (X^2\Sigma_g^+)$, we have measured the rotational and fine-structure level-specific linewidths in $v=0$ and $v=2$ of the $B^3\Sigma_u^-$ state. These linewidths represent the first measurement of fine-structure level-specific predissociation rates in $B^3\Sigma_u^-$ ($v<10$), and they are found to vary considerably among the various rotational and fine-structure levels, encompassing a range of 0.09–0.34 cm$^{-1}$ in $v=0$, $N'=4$, and 0.4–1.4 cm$^{-1}$ in $v=2, N'=4$. Orbit-rotational coupling in the $B^3\Sigma_u^-\rightarrow 1\Pi_u$ interaction, in addition to spin-orbit coupling in the $B^3\Sigma_u^--1\Pi_u, 3\Pi_u$ interactions, is found to be crucial to explaining the relative predissociation rates among the fine-structure levels, even in low rotational levels. Measurements were made in the $(\nu',\nu'')=(0,0), (0,1), (0,2), (1,0), (1,2), (0,21)$ Schumann–Runge $[B^3\Sigma_u^-\nu')-X^2\Pi_g^-\nu'\nu'\nu'']$ bands without presumption as to the molecular constants in either the $X$ or $B$ states. The use of high ground state vibrational levels as a starting point for the photoexcitation measurements produces a spectral separation among the previously blended triplet components of the absorption lines. All lines in these bands are found to be broadened by predissociation, with those terminating in $\nu'=0$ and in the $N'=J'-1$ ($F'_{1,2}$) levels exhibiting the smallest effect.

I. INTRODUCTION

Due to the importance of the $\text{O}_2$ Schumann–Runge (SR) system $[B^3\Sigma_u^-\nu')-X^2\Pi_g^-\nu'\nu'\nu'\nu'\nu'\nu'\nu'\nu']$ in atmospheric absorption and in flame diagnostic experiments, much recent work has gone into understanding the spectroscopy of this transition. The SR system is particularly interesting because the upper level is strongly predissociated by a number of repulsive $\text{O}_2$ states, as may be seen in Fig. 1. Thus each vibrational level behaves in a different manner in terms of predissociative linewidths, and hence radiative efficiencies. Not only are the linewidths dependent on vibrational level, but they also are rotational-level dependent.

There are now numerous compilations, both theoretical and experimental, of the linewidths for almost the full range of $\text{O}_2 (B)$ vibrational levels, but a very important member of this set is the $\nu'=0$ level, for which there is little information. The reason is that most measurements are made in absorption from the $\nu'=0$ level, and the Franck–Condon factor for the $\text{SR}(\nu',\nu'')=(0,0)$ band is quite small, the calculated value being on the order of $10^{-5}$. Cheung et al. have made some high-pressure measurements, but in that case the lines are pressure broadened and the results have been somewhat inconclusive. Julienne has calculated a predissociation line width of 0.06 cm$^{-1}$ for $\nu'=0$, and as a result it has been generally felt that emission studies are best carried out with this level, since it should be the most efficient radiator of the lower vibrational levels by a substantial margin. However, Cheung et al. argue that their own study points to a significantly higher value for the $\nu'=0$ linewidth, which, if correct, reduces the difference between this level and the others. We note that emission measurements (e.g., laser-induced fluorescence (LIF) techniques) have, until now, not been used successfully as a way of obtaining the $\nu'=0$ linewidth because of the problem of exciting $\nu'=0$ in a nonflame environment, and also because of the difficulty in dispersing the fine structure in this $B^3\Sigma_u^-\rightarrow X^2\Pi_g^-$ transition.

An applied area where questions about the SR linewidths are of great concern is solar photoabsorption. The depth of penetration of 130–210 nm solar radiation into the atmosphere depends on the $\text{O}_2$ absorption cross sections, and in the 40–90 km altitude range, absorption by the SR bands is particularly important. Whereas all solar radiation in this wavelength region is ultimately absorbed, the details are critical in determining the altitude profiles for photoabsorption.
O$_2$(X,v=8-22) 300 K quenching rate coefficients for O$_2$ and N$_2$, and O$_2$(x) vibrational distribution from 248 nm O$_3$ photodissociation

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Vibrationally excited oxygen (O$_3$) is produced in the atmosphere by ozone photodissociation in the 200-300 nm Hartley band. It has been suggested that photoexcitation of O$_3$ in the O$_3$ Schumann-Runge bands will lead to predissociation, and autocatalytic production of O$_2$. The resultant new source of atmospheric O$_3$ could help alleviate current discrepancies between observed and modeled O$_3$ profiles. To evaluate this possibility, we have examined two critical factors—the nascent distribution of O$_3$ levels for 248 nm photodissociation, near the peak of the Hartley band, and the rate coefficients for their relaxation by O$_3$ and N$_2$. We find that the distribution extends to v=22, close to the thermodynamic limit, with a peak near v=3. The 300 K quenching rate coefficients have been evaluated using a cascade model, in which it is assumed that relaxation by O$_3$ occurs through single-quantum vibration-vibration (V-V) and vibration-translation (V-T) steps. By modeling the relaxation from the top of the distribution downwards, we simultaneously obtain both the quenching rate coefficients and the nascent vibrational distribution. Agreement with rate coefficient measurements carried out in a state-specific manner is good, as is also true for the comparison with new V-V and V-T calculations. Data from experiments on O$_3$ quenching by N$_2$ show that in the v=16-22 range, potentially important in the atmosphere, quenching proceeds up to five times faster than for the case of O$_3$. The hypothesized explanation is that two-quantum V-V transfer, peaking at the resonant condition of O$_3$(v=18-19), is the dominant process. As a consequence, atmospheric quenching of O$_3$ for levels above v=14 is basically controlled by N$_2$, and at low stratospheric temperatures, the effect of N$_2$ quenching near v=18 is likely to be 2 orders of magnitude greater than quenching by O$_3$. This unexpected effect probably precludes a significant role for O$_3$ photodissociation as a new source of stratospheric O$_3$, but the existence of these high-energy entities can have other consequences, among them being enhanced activity with minor species, and the possibility that energy may flow from the relatively stable O$_2$ (v=1) and N$_2$(v=1) levels into infrared-active H$_2$O and CO$_2$, respectively. Measurements have also been made for O$_3$ quenching by O$_3$, CO$_2$, and He, particularly to establish whether O$_3$ and CO$_2$ can play a competitive quenching role in the atmosphere. Although O$_3$ is a fast quencher, with CO$_2$ being 2 orders of magnitude slower, they are unlikely to compete with O$_3$ and N$_2$. The data on He is particularly interesting, suggesting that considerably more O$_3$ is present in the nascent O$_3$ photodissociation products than subsequently appears from O$(^1D)$+O$_3$ interaction. The implications of this finding are discussed.

I. INTRODUCTION

The role of vibrationally excited air molecules in atmospheric chemistry is an issue that has been long debated, and there are many ways in which O$_3$, N$_2$, and NO$^+$ can be generated in disturbed or even quiescent atmospheres. Of these, only NO$^+$ has been extensively studied, because it is infrared active. Hypotheses concerning O$_3$ and N$_2$ have to a large extent gone unexplored because two species cannot be directly detected in the atmosphere. Nevertheless, questions concerning non-LTE (local thermodynamic equilibrium) processes continue to arise, and it is essential that an experimental data base be developed to describe the kinetic behavior of O$_3$ (and N$_2$) over a large range of vibrational levels and temperatures. That has been the thrust of our program to explore kinetic parameters for O$_3$.

The work of Fairchlld et al. and Sparks et al. had established that when ozone is photodissociated in the Hartley band, there is a triplet channel

$$O_3 + hv = O(^1P) + O_2(X^3\Sigma^+ , v)$$

in addition to the predominant singlet channel,

$$O_3 + hv = O(^1D) + O_2(a^1\Delta_g).$$

The yield into the singlet channel is typically 0.9 over the 240-300 nm range, and a 0.1 yield is therefore accepted for the triplet channel. In the two studies mentioned above, it was ascertained that vibrational excitation in the product O$_3$ extended to at least v=10. Thus, the study of ozone photodissociation is potentially valuable both as a problem in atmospheric photodissociation dynamics, and for its relevance to investigations of vibrationally excited O$_3$.

In the course of investigating possible new atmospheric sources of ozone, Slangen et al. discovered that irradiation of O$_3$ at the KrF excimer laser wavelength of 248 nm produced ozone. Since the O$_3$ photodissociation threshold is 242 nm, the origin of the ozone was not clear, but it was

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Energetic Molecular Oxygen in the Atmosphere

Tom G. Slanger

Industrialized nations now devote a substantial part of their atmospheric research to studies of ozone photochemistry. These studies have emphasized ways in which ozone loss has been accelerated by human activity. Relatively little attention, however, has been paid to the details of how atmospheric ozone is created. In the research article by Miller et al. on page 1831 of this issue (1), a mechanism is proposed for atmospheric ozone production—namely, reaction between highly vibrationally excited $\text{O}_2$ and ground-state $\text{O}_3$—that may have relevance to the overall ozone balance. The standard view is that solar radiation at wavelengths shorter than 242 nm photodissociates oxygen, and the resultant atoms form ozone by $\text{O} + \text{O}_2$ three-body recombination. However, the devil is in the details, and we know that the atmosphere is a stew (admittedly dilute) of high-energy particles. This is particularly true for oxygen and its allotropes (see figure). Note that the products of direct ozone photodissociation are not necessarily distinguishable from those originating with $\text{O}_3$. Thus, ozone photodissociation, usually viewed as a do-nothing process in terms of changing the ozone balance, can have a significant effect in this regard, particularly because ozone photodissociation rates are far larger than those for oxygen.

Life on Earth is protected from ultraviolet radiation in the range of 200 to 310 nm by stratospheric ozone photodissociation and dissociation

\[
\text{O}_2 + h\nu (200 - 310 \text{ nm}) \rightarrow \text{O}(1D) + \text{O} \quad (a^3\Delta_u) \quad -90\% \quad (1a)
\]

\[
\text{O}(1D) + \text{O} \rightarrow \text{O}_2(a^3\Sigma_u^+) \quad -10\% \quad (1b)
\]

$\text{O}(1D)$ is quenched rapidly by all collision partners and is the single most important intermediate in the atmosphere because it is responsible for generating several molecules (CH, NO, and CH$_3$) whose subsequent reactions in a sense define stratospheric chemistry. Early attempts at atmospheric ozone modeling—based only on $\text{O}_3$, $\text{O}_3$, and $\text{O}_3$ chemistry—did not consider these minor components, and only when the importance of the HO, and NO, catalytic cycles was recognized did modeled ozone profiles fall into reasonable agreement with observation. This evolving process continues with the addition of the $\text{ClO}$ cycle and $\text{ClO}_3$ chemistry in the Antarctic, and as a more precise understanding of ozone photochemistry becomes necessary, attention shifts to more transient species.

Until recently, the channel shown in reaction 1b, giving ground-state products, was ignored, on the assumption that vibrationally excited oxygen would innocuously convert its energy into heat. However, the extent of vibrational excitation was not fully appreciated, and it now appears that this entity may have interesting chemical properties in terms of ozone production. In theory, these active $\text{O}_3$ molecules could have a substantial impact on atmospheric chemistry in that they are copiously produced and, unlike $\text{O}(1D)$, are not rapidly quenched by $\text{O}_3$ and $\text{N}_2$.

The interest in new ozone sources arises because current models of altitude-dependent ozone concentration profiles underestimate the amount of ozone actually present in the higher atmosphere (above the region affected by chlorofluorocarbon chemistry). The discrepancy is 10 to 20$\%$ at altitudes of 40 to 70 km, being larger at the higher altitude (2), and has become known as the "ozone deficit problem."

The article by Miller et al. (1) proposes a new way by which ozone may be generated and addresses the question of the ozone deficit. In this study, imaging techniques combined with resonant multiphoton ionization (REMPI) are used to measure the translational energy of ground-state oxygen atoms produced from the 226-nm photodissociation of ozone. From such a measurement, the internal energy of the accompanying ground-state $\text{O}_3$ fragment can be deduced, and the authors find that vibrationally excited $\text{O}_3$, where $v$ is the level of vibrational excitation, is produced up to the limit of available energy, $v = 17$, for 226-nm dissociation. This is consistent with our finding that $\text{O}_2(v)$ is produced up to $v = 12$ as a result of 248-nm photodissociation of ozone (3, 4).

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Ovenish detailed. A partial diagram of oxygen isotope cycles in an $\text{O}_2$-M system that has been subjected to solar radiation, including both confirmed and proposed reaction pathways (M = $\text{O}_2$, $\text{N}_2$). Electronic states of $\text{O}$ and $\text{O}_3$ are shown at right.

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Branch intensities and oscillator strengths for the Herzberg absorption systems in oxygen

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This paper is dedicated to Dr. Gerhard Herzberg on the occasion of his 90th birthday

We report two complementary experimental investigations of the absorption spectrum of molecular oxygen between 243 and 258 nm. In the first experiment, excitation of O$_3$ is inferred by detecting oxygen atoms resulting from chemical reaction. In the second experiment, absorption by O$_3$ is observed directly by cavity ring-down spectroscopy. Absorption strengths for the Herzberg I ($4^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$), Herzberg II ($4^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$), and Herzberg III ($4^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$) band systems are modeled with the DIATOM spectral simulation computer program using the best available branch intensity formulas. Absolute oscillator strengths are derived for all three systems and compared with values in the literature.

Table 1. Forbidden transitions in O$_3$

<table>
<thead>
<tr>
<th>Transition</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>$4^3\Sigma_u^+$</td>
<td>Herzberg I</td>
</tr>
<tr>
<td>$4^1\Sigma_u^+$</td>
<td>Herzberg II</td>
</tr>
<tr>
<td>$4^3\Delta_g$</td>
<td>Herzberg III</td>
</tr>
<tr>
<td>$4^3\Sigma_u^+$</td>
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<tr>
<td>$4^1\Delta_g$</td>
<td>Infrared-Atmospheric</td>
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</table>

Table 1. Forbidden transitions in O$_3$

1. Introduction

The forbidden transitions of molecular oxygen play conspicuous roles in understanding the earth's atmosphere [1-5] and offer special challenges to the spectroscopist. Among the six spectroscopically known bound states that result from association of ground state oxygen atoms, $X^1\Sigma_g^+$, $a^1\Sigma_g^+$, $b^1\Sigma_g^+$, $c^1\Pi_g$, $A^3\Delta_u$, and $A^3\Sigma_u^+$, there are 15 possible radiative transitions, all of which are forbidden. Eight of these transitions have been observed (see Table 1), all terminating either on the ground or the first excited state. All of the five transitions terminating on the ground state are associated with the work of Gerhard Herzberg, and three carry his name in their designation.

1.1. Line positions and branch intensities

The transition $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ in O$_3$ has a long and distinguished history, beginning with its discovery by Herzberg in 1932 [6], which in turn led to its designation of "Herzberg I," being the first of the three 240-260 nm absorption systems in O$_3$ that he studied. As remarked by Present [7], the appearance of this spectrum is unusual in that at moderate resolution it consists of three Q-form branches, of approximate relative strength of 2:1:2. As the resolution and sensitivity are improved [8, 9], the three strong Q-form branches are resolved into five branches of nearly equal strength, plus one weak satellite Q-form branch on each side, in addition to three weak S-form and three weak O-form branches on the blue and red sides, respectively.

In the present study we have calculated the branch strengths for O$_3$ $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition. Present [7] considered the possibility of mixing of either the upper or lower state with a $3^1\Pi_g$ state by either spin-orbit or rotational coupling. Choosing one of these two coupling mechanisms gives an intensity distribution with some strong Q-form branches, and weaker O-form and S-form branches, but neither is satisfactory [8]. In our earlier paper [10] on the $A^3\Sigma_u^+ \rightarrow a^1\Delta_g$ transition, we showed a simulation of the $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ transition that included a new source of transition probability, spin-orbit mixing of $A^3\Sigma_u^+$ with the well-known $3^1\Pi_g$ state, in addition to spin-orbit mixing of an unspecified $3^1\Pi_g$ state with $X^1\Sigma_g^+$. That simulation was a significant improvement over the previous attempts, but quantitive results are obtained only by including all three perturbations. Even though the rotational mixing with the $3^1\Pi_g$ state makes a minor contribution to the total transition probability, its alternate constructive and destructive interference with the stronger spin-orbit-induced contributions has a profound influence on the relative strengths of the branches. Our work was described in a conference presentation [11]. Similar ideas have been developed and documented by Lewis and Gibson [12], modified by Cann and Nicholls [13], and applied qualitatively to the Herzberg I transition.
PHOTOABSORPTION IN THE 40950–41300 CM\(^{-1}\) REGION; NEW HERZBERG BANDS, NEW ABSORPTION LINES, AND IMPROVED SPECTROSCOPIC DATA

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ABSTRACT

The technique of cavity ring-down (CRD) spectroscopy is particularly useful for measuring absorptions of very weak optical transitions. We have in this manner investigated the 40950–41300 cm\(^{-1}\) region in O\(_2\), where only absorption in the O\(_2\)(A\(^3\)\(\Sigma^+\) - X\(^3\)\(\Sigma^+\)) 11-0 band had been previously identified. Five new bands have been discovered in this range - the A\(^3\)\(\Delta_u\) - X\(^3\)\(\Sigma^+\) 12-0 and 13-0 bands, the c\(^1\)\(\Sigma^+_u\) - X\(^3\)\(\Sigma^+\) 17-0 and 18-0 bands, and the A\(^3\)\(\Sigma^+\) - X\(^3\)\(\Sigma^+\) 12-0 band. The origins of the F\(_1\) and F\(_2\) components of the latter lie only 7 cm\(^{-1}\) below the lowest dissociation limit, and 15 lines have been identified. No F\(_3\) levels were observed; apparently all are above the dissociation limit. The high instrumental sensitivity of the CRD technique has allowed observation of weak lines of the A-X 11-0 band, and 12 of the 13 branches have been identified and their intensities measured. A very low upper limit has been set on the intensity of the thirteenth branch, Q\(_{13}\). We find 107 unidentified lines in the region, the stronger ones (19) lying in the vicinity of lines of the A-X 11-0 band.

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MEASUREMENTS OF O$_2$ SCHUMANN-RUNGE BAND LINEWIDTHS: B$^3\Sigma_u^+(v=0-2,13-16)$

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ABSTRACT

Absorption linewidths have been measured at high resolution in 17 bands of the O$_2$ B$^3\Sigma_u^-$ $\leftarrow$ X$^3\Sigma_g^-$ Schumann-Runge band system using laser-induced fluorescence techniques. These measurements access $v'$ = 0, 1, 2, 13, 14, 15, and 16 of the B state with a complete resolution of its triplet fine structure. In order to achieve this resolution, and to minimize Doppler contributions to the lineshape, excitation to the B state is made from high vibrational levels of the O$_2$ ground state, X$^3\Sigma_g^-(v = 9,10,19,20,21,22,26,27)$, which are produced by the reaction of O(1D) with O$_3$. Measured absorption lines are fitted to a Voigt lineshape to separate the inhomogenous contributions (laser line shape, Doppler width) from the homogenous contribution due to predissociation lifetime. The observed homogenous contributions, which range from 0.05 cm$^{-1}$ for the $v'$ = 14, N=24, F$_1$ level to 1.2 cm$^{-1}$ for the $v'$ = 1, N = 16, F$_2$ level, are strongly dependent on vibrational, rotational, and fine-structure quantum number, reflecting a complex interplay of the couplings between the B state and the repulsive O$_2$ states arising from the lowest separated-atom limit, O$^3P$ + O$^3P$. Comparison of the present measurements to the homogeneous linewidths predicted by the recent refinement [B. R. Lewis et al., J. Chem. Phys. 100, 7012 (1994)] to the Jullienne and Krauss [P. S. Julienne and M. Krauss, J. Mol. Spectrosc. 56, 270 (1975)] predissociation model finds near-quantitative agreement for B state levels in $v'$ = 0,1,2, and 15, but systematic differences in $v'$ = 13 and 14. This suggests that an additional refinement of the predissociation model should be made, taking into account the high resolution measurements now available in the higher vibrational levels of the B state.
REVISED TRANSITION PROBABILITIES FOR THE O₂ HERZBERG BAND SYSTEMS

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ABSTRACT

The transition probabilities associated with the O₂ Herzberg systems ($A^3Σ_u^- - X^1Σ_g^+$, $A^3Δ_u - X^1Σ_g^+$, $c^1Σ_u^- - X^1Σ_g^+$) have suffered from considerable uncertainty. Bates [1989] tabulated the transition arrays, based on theoretical calculations of the transition moments by Klotz and Peyerimhoff [1986], but the relative values for the three systems did not fit well with the fragmentary existing absorption information. Recent experimental studies have produced more quantitative data, and we present new tabulations for the three systems. The transitions are weaker than Bates has indicated, by a factor of about 1.5 for the $A-X$ system, and 2-3 for the $c-X$ system. New and old absorption spectra have been used to develop internal consistency between the O₂ systems.