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ATMOSPHERIC OXYGEN PHOTOABSORPTION

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CONTENTS

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 O_2 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 O_2 absorption, since absorption in the $B^3\Sigma_u^- - X^3\Sigma_g^-$ 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,[1] in which only the v = 0 and v = 2 levels of the $B^3\Sigma_u^-$ 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 $B^3\Sigma_u^-$ 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,[2,3] 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 O_2 levels, provides us with an enormous O_2(vib) distribution: v = 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 O_2, N_2, O_3, CO_2, and He as quenchers.[4] An early premise of ours,[5] that solar radiation could play a role in photodissociating O_2(vib), was shown to be incorrect, because quenching by O_2 and N_2 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 O_2 exhibited a minimum near v = 19, where $V \rightarrow T$ quenching takes over from $V \rightarrow V$. An important observation is that there is a resonance between the fundamental N_2 vibrational quantum and two O_2 quanta near v = 19. Thus, the N_2 quenching rate coefficients show a peak in this region and dominate the O_2 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 O_2(vib).

These latter researchers found an interesting effect that sets in at $O_2(v = 26)$ in the quenching of $O_2(v)$ by O_2,[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.[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 $O_2(A^3\Sigma_u^+)$ 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,[16] ultimately concluding that the current Herzberg continuum cross sections of Yoshino et al.[17] and an older set of Herzberg I cross sections by Hasson et al.[18] are the most compatible and best represent the true state of affairs. A new paper by Amoruso et al.[19] has muddied the waters by reporting continuum cross section values lower than those of Yoshino et al.,[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 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.[20] The new A state level, v = 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 O_2. There are weakly bound states that have long been proposed as potentially important in the atmosphere,[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.[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.[25]

PUBLICATIONS RESULTING FROM THIS GRANT

P. C. Cosby, H. Park, R. A. Copeland, and T. G. Slanger, "Predissociation Linewidths in $O_2(B^3\Sigma_u^-)$, v = 0,2," J. Chem. Phys. **98**, 5117 (1993).

H. Park and T. G. Slanger, "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," J. Chem. Phys. **100**, 287 (1994).

T. G. Slanger, "Energetic Molecular Oxygen in the Atmosphere," Science **265**, 1817 (1994).

D. L. Huestis, R. A. Copeland, K. Knutsen, T. G. Slanger, R. T. Jongma, M.G.H. Boogarts, and G. Meijer, "Branch Intensities and Oscillator Strengths for the Herzberg Absorption Systems in Oxygen," Can. J. Phys. **72**, 1109 (1994).

T. G. Slanger, D. L. Huestis, P. C. Cosby, H. Naus, and G. Meijer, "O_2 Photoabsorption in the 40950-41300 cm^{-1} Region: New Herzberg Bands, New Absorption Lines, and Improved Spectroscopic Data," J. Chem. Phys. **105**, in press (1996).

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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 O_2," J. Geophys. Res. (in preparation).

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APPENDICES

A-1 P. C. Cosby, H. Park, R. A. Copeland, and T. G. Slanger, "Predissociation Linewidths in $O_2(B^3\Sigma_u^-)$, v = 0,2," J. Chem. Phys. **98**, 5117 (1993).

A-2 H. Park and T. G. Slanger, "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," J. Chem. Phys. **100**, 287 (1994).

A-3 T. G. Slanger, "Energetic Molecular Oxygen in the Atmosphere," Science **265**, 1817 (1994).

A-4 D. L. Huestis, R. A. Copeland, K. Knutsen, T. G. Slanger, R. T. Jongma, M.G.H. Boogarts, and G. Meijer, "Branch Intensities and Oscillator Strengths for the Herzberg Absorption Systems in Oxygen," Can. J. Phys. **72**, 1109 (1994).

A-5 T. G. Slanger, D. L. Huestis, P. C. Cosby, H. Naus, and G. Meijer, "O_2 Photoabsorption in the 40950-41300 cm^{-1} Region: New Herzberg Bands, New Absorption Lines, and Improved Spectroscopic Data," J. Chem. Phys. **105**, in press (1996).

A-6 P. C. Cosby, J. M. Price, and T. G. Slanger, "Measurements of O_2 Schumann-Runge Band Linewidths: $B^3\Sigma_u^-$ (v = 0-2,13-16)," J. Chem. Phys. (in preparation).

A-7 D. L. Huestis, P. C. Cosby, and T. G. Slanger, "Revised Transition Probabilities for the O_2 Herzberg Band Systems," J. Geophys. Res. (in preparation).

Predissociation linewidths in 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 $O_2(X^3\Sigma_g^-)$, 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 $v=0$, $N'<36$, and 0.4–1.4 cm^{-1} in $v=2$, $N'<24$. Orbit-rotational coupling in the $B^3\Sigma_u^- - {}^3\Pi_u$ interaction, in addition to spin-orbit coupling in the $B^3\Sigma_u^- - {}^1\Pi_u$, $-{}^3\Pi_u$, $-{}^5\Pi_u$ 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 $(v',v'')=(0,9)$, $(0,10)$, $(0,21)$, $(2,10)$, and $(2,22)$ Schumann–Runge $[B^3\Sigma_u^-(v')-X^3\Sigma_g^-(v'')]$ 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 $v'=0$ and in the $N'=J'-1$ (F'_1) levels exhibiting the smallest effect.

I. INTRODUCTION

Due to the importance of the O_2 Schumann–Runge (SR) system $[B^3\Sigma_u^-(v')-X^3\Sigma_g^-(v'')]$ in atmospheric absorption and in flame diagnostic experiments, much recent work has gone into understanding the spectroscopy of this transition.[1-29] The SR system is particularly interesting because the upper level is strongly predissociated by a number of repulsive 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 $O_2(B)$ vibrational levels,[4-9,15-21,29] but a very important member of this set is the $v'=0$ level, for which there is little information. The reason is that most measurements are made in absorption from the $v''=0$ level, and the Franck–Condon factor for the $SR(v',v'')=(0,0)$ band is quite small, the calculated value[30] being on the order of 10^{-9}. Cheung *et al.*[15] have made some high-pressure measurements, but in that case the lines are pressure broadened and the results have been somewhat inconclusive. Julienne[4] has calculated a predissociation line width of 0.06 cm^{-1} for $v'=0$, 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.*[15] argue that their own study points to a significantly higher value for the $v'=0$ 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 $v'=0$ linewidth because of the problem of exciting $v'=0$ in a nonflame environment, and also because of the difficulty in dispersing the fine structure in this ${}^3\Sigma_u^- - {}^3\Sigma_g^-$ 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 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 photo-

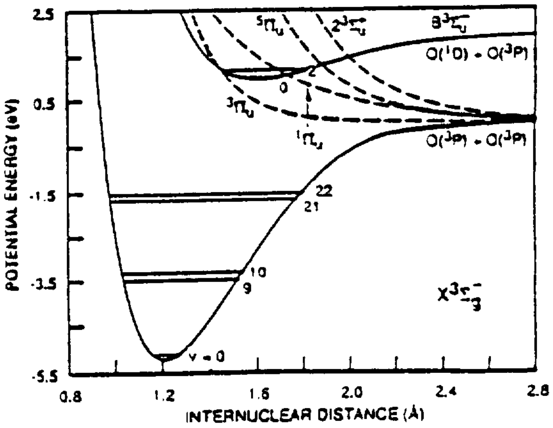

FIG. 1. Potential energy curves of the relevant electronic states in O_2. Predissociation of the $B^3\Sigma_u^-$ state is produced by the four continuum states shown by the dashed curves in the figure. Almost all previous information on B-state predissociation has derived from $B-X$ absorption band measurements originating in $v=0$ of the $X^3\Sigma_g^-$ state. The present measurements access $B(v=0,2)$ from $X(v=9,10,21,22)$. These vibrational levels are shown by solid horizontal lines in the figure.

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$O_2(X,v=8-22)$ 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 ($O_2^\ddagger$) is produced in the atmosphere by ozone photodissociation in the 200–300 nm Hartley band. It has been suggested that photoexcitation of $O_2^\ddagger$ in the O_2 Schumann–Runge bands will lead to predissociation, and autocatalytic production of O_3. 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 $O_2^\ddagger$ levels for 248 nm photodissociation, near the peak of the Hartley band, and the rate coefficients for their relaxation by O_2 and N_2. We find that the distribution extends to $v=22$, close to the thermodynamic limit, with a peak near $v=8$. The 300 K quenching rate coefficients have been evaluated using a cascade model, in which it is assumed that relaxation by O_2 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 new 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 $O_2^\ddagger$ 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_2. The hypothesized explanation is that two-quantum $V-V$ transfer, peaking at the resonant condition of $O_2(v=18–19)$, is the dominant process. As a consequence, atmospheric quenching of $O_2^\ddagger$ 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_2. This unexpected effect probably precludes a significant role for $O_2^\ddagger$ 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_2O and CO_2, respectively. Measurements have also been made for $O_2^\ddagger$ 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_2 and N_2. The data on He is particularly interesting, suggesting that considerably more $O_2^\ddagger$ 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 $O_2^\ddagger$, $N_2^\ddagger$, and $NO^\ddagger$ can be generated in disturbed or even quiescent atmospheres. Of these, only $NO^\ddagger$ has been extensively studied, because it is infrared active.[1] Hypotheses concerning $O_2^\ddagger$ and $N_2^\ddagger$ have to a large extent gone unexplored because these 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 $O_2^\ddagger$ (and $N_2^\ddagger$) over a large range of vibrational levels and temperatures. That has been the thrust of our program to explore kinetic parameters for $O_2^\ddagger$.

The work of Fairchild *et al.*[2] and Sparks *et al.*[3] had established that when ozone is photodissociated in the Hartley band, there is a triplet channel

$$O_3+h\nu\rightarrow O(^3P)+O_2(X\,^3\Sigma_g^-,v) \tag{1}$$

in addition to the predominant singlet channel,

$$O_3+h\nu\rightarrow O(^1D)+O_2(a\,^1\Delta_g). \tag{2}$$

The yield into the singlet channel is typically 0.9 over the 240–300 nm range,[4] 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_2 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_2.

In the course of investigating possible new atmospheric sources of ozone, Slanger *et al.*[5] discovered that irradiation of O_2 at the KrF excimer laser wavelength of 248 nm produced ozone. Since the O_2 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

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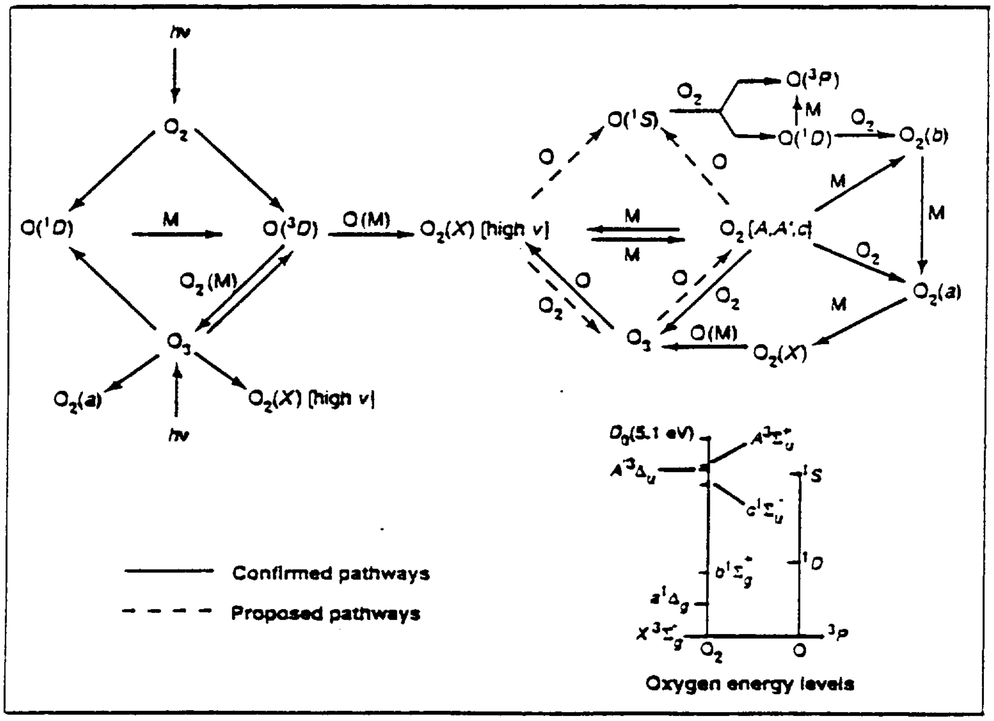
Industrialized nations now devote a substantial part of their atmospheric research to studies of ozone photochemistry. These studies have emphasized ways in which ozone loss has been accelerated by human activity. Relatively little attention, however, has been paid to the details of how atmospheric ozone 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 O_2 and ground-state O_2—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 $O + O_2$ 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 O_2. 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 photoabsorption rates are far larger than those for oxygen.



Devilish details. A partial diagram of oxygen allotrope cycles in an O_2-M system that has been subjected to solar radiation, including both confirmed and proposed reaction pathways (M = O_2, N_2). Electronic states of O and O_2 are shown at right.

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

$$O_3 + h\nu(200-310\ \text{nm})$$

$$\rightarrow O(^1D) + O_2(a^1\Delta_g)\ \sim 90\% \qquad (1a)$$

$$\rightarrow O(^3P) + O_2(X^3\Sigma_g^-)\ \sim 10\% \qquad (1b)$$

$O(^1D)$ 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 (OH, NO, and CH_3) whose subsequent reactions in a sense define stratospheric chemistry. Early attempts at atmospheric ozone modeling—based only on O, O_2, and O_3 chemistry—did not consider these minor components, and only when the importance of the HO_x and NO_x catalytic cycles was recognized did modeled ozone profiles fall into reasonable agreement with observation. This evolving process continues with the addition of the ClO_x cycle and $(ClO)_2$ 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 O_2 molecules could have a substantial impact on atmospheric chemistry in that they are copiously produced and, unlike $O(^1D)$, are not rapidly quenched by O_2 and 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 O_2 fragment can be deduced, and the authors find that vibrationally excited O_2—$O_2(v)$, where *v* is the level of vibrational excitation—is produced up to the limit of available energy, $v = 27$, for 226-nm dissociation. This is consistent with our finding that $O_2(v)$ is produced up to $v = 22$ as a result of 248-nm photodissociation of ozone (*3*, *4*).

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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_2 is inferred by detecting oxygen atoms resulting from chemical reaction. In the second experiment, absorption by O_2 is observed directly by cavity ring-down spectroscopy. Absorption strengths for the Herzberg I ($A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$), Herzberg II ($c^1\Sigma_u^- \leftarrow X^3\Sigma_g^-$), and Herzberg III ($A'^3\Delta_u \leftarrow X^3\Sigma_g^-$) 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.

Nous présenton deux investigations complémentaires du spectre d'absorption de l'oxygène moléculaire entre 243 et 258 nm. Dans la première expérience, l'excitation de O_2 est inférée par la détection d'atomes d'oxygène provenant de réactions chimiques. Dans la seconde, l'absorption par O_2 est observée directment dans une cavité ("cavity ring-down spectroscopy"). Les forces d'absorption pour les systèmes de bandes Herzberg I ($A^3\Sigma_u^+ \leftarrow X^3\Sigma_g^-$), Herzberg II ($c^1\Sigma_u^- \leftarrow X^3\Sigma_g^-$) et Herzberg III ($A'^3\Delta_u \leftarrow X^3\Sigma_g^-$) sont modélisées avec le programme DIATOM de simulation spectrale par ordinateur, en utilisant les meilleures formules disponibles pour les intensités des branches. Les forces d'oscillateurs absolues sont calculées et comparées avec les valeurs rapportées dans la littérature.

[Traduit par la rédaction]

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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, $X^3\Sigma_g^-$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, $A'^3\Delta_u$, 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 on either 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.

TABLE 1. Forbidden transitions in O_2

	$X^3\Sigma_g^-$	$a^1\Delta_g$
$A^3\Sigma_u^+$	Herzberg I	(Unobserved)
$A'^3\Delta_u$	Herzberg III	Chamberlain
$c^1\Sigma_u^-$	Herzberg II	Richards–Johnson
$b^1\Sigma_g^+$	Atmospheric	Noxon
$a^1\Delta_g$	Infrared-atmospheric	

1.1. Line positions and branch intensities

The transition $A^3\Sigma_u^+ - X^3\Sigma_g^-$ in O_2 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_2 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 first attempt to calculate the branch strengths for O_2 $A^3\Sigma_u^+ - X^3\Sigma_g^-$, Present [7] considered the possibility of mixing of either the upper or lower state with a $^3\Pi$ 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 $A'^3\Delta_u \rightarrow a^1\Delta_g$ transition, we showed a simulation of the $A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ transition that included a new source of transition probability, spin-orbit mixing of $A^3\Sigma_u^+$ with the well-known $B^3\Sigma_u^-$ state, in addition to spin-orbit mixing of an unspecified $^3\Pi_g$ state with $X^3\Sigma_g^-$. That simulation was a significant improvement over the previous attempts, but quantitative results are obtained only by including all three perturbations. Even though the rotational mixing with the $^3\Pi$ 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.

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O_2 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 $O_2(A^3\Sigma_u^+ - X^3\Sigma_g^-)$ 11-0 band had been previously identified. Five new bands have been discovered in this range - the $A'^3\Delta_u - X^3\Sigma_g^-$ 12-0 and 13-0 bands, the $c^1\Sigma_u^- - X^3\Sigma_g^-$ 17-0 and 18-0 bands, and the $A^3\Sigma_u^+ - X^3\Sigma_g^-$ 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: $B^3\Sigma_u^-(v=0\text{-}2,13\text{-}16)$

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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, rotatational, 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 O_2 HERZBERG BAND SYSTEMS

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ABSTRACT

The transition probabilities associated with the O_2 Herzberg systems ($A^3\Sigma_u^+$-$X^3\Sigma_g^-$, $A'^3\Delta_u$-$X^3\Sigma_g^-$, $c^1\Sigma_u^-$-$X^3\Sigma_g^-$) 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 O_2 systems.