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O_2 HERZBERG STATE REACTION WITH N_2: A POSSIBLE SOURCE OF STRATOSPHERIC N_2O

Tom G. Slanger and Richard A. Copeland
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SRI Project PYU 1205
Contract No. NAG2-1022
MP 97-034

Prepared for:

NASA-Ames Research Center
MS 245-4
Moffett Field, CA 94035-1000

Attn: Estelle P. Condon

APR 24 1997

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SUMMARY

The goal of this one-year investigation was to determine whether N_2O is formed in atmospherically significant quantities by the reaction of vibrationally excited levels of the $O_2(A^3\Sigma_u^+)$ state with nitrogen. $O_2(A^3\Sigma_u^+)$ is made throughout the upper stratosphere in considerable amounts by solar photoabsorption, and only a very small reactive yield is necessary for this mechanism to be a major N_2O source.

By long-term 245-252 nm irradiation of O_2/N_2 mixtures on- and off-resonance with absorption lines in the $O_2(A^3\Sigma_u^+ - X^3\Sigma_g^-)$ transition, followed by N_2O analysis by frequency-modulated diode laser absorption spectroscopy, we determined an upper limit for the N_2O yield of the candidate reaction. This limit, 3×10^{-5}, eliminates $O_2(A^3\Sigma_u^+) + N_2$ as a significant channel for the generation of stratospheric N_2O.

In further measurements, we established that N_2O is stable under our photolysis conditions, showing that the small amounts of ozone generated from the reaction of $O_2(A)$ and O_2 do not indirectly lead to destruction of N_2O.

BACKGROUND

Current models of stratospheric N_2O rely on ground-based sources (natural or anthropogenic) to supply the N_2O found in the stratosphere. N_2O is a very long-lived species, with an estimated residence time in the atmosphere of 90-120 years. Its principal method of destruction is photodissociation. The balance of known sources and sinks of N_2O is not yet in a satisfactory state, with the sinks outweighing the sources by about 30% in most models.

This perceived imbalance has been interpreted as evidence of an unaccounted source in the atmosphere, but such an argument for a new source is not persuasive when considered alone, because the bookkeeping parameters are still evolving. Stronger evidence arises from observations of isotope fractionation, where analysis of stratospheric air shows that the heavier O and N isotopes are enhanced in a mass-independent manner over what is found at ground level.[1,2] These observations suggest that at least some of the N_2O in the stratosphere does not originate at the ground, and that there is an isotopically selective *in situ* source.

Attempts to define such a source have been made at various times, and the fact that the components of the N_2O molecule exist in the air itself (i.e., N_2 and O_2) has led researchers to wonder how N_2O might be formed by air chemistry, with the sun as the energy source. Zipf and

Prasad[3] considered the photoexcitation of N_2 followed by reaction with O_2 as a possible N_2O source and they are now considering the reaction of the transient $O_2(B^3\Sigma_u^-)$ state with N_2.[4]

In our recently completed work, more fully described in the Appendix, we investigated whether solar pumping of the $O_2(A^3\Sigma_u^+)$ state, which we recently showed to be rapidly removed in collision with N_2, can be an N_2O source. Because the $O_2(A)$ production rate is quite large, the necessary reactive yield for $O_2(A) + N_2$ to be an interesting N_2O source is small; we initially proposed that a yield greater than 4×10^{-4} would be significant compared with known sources.

The challenge in these experiments has been to measure very small amounts of N_2O and to eliminate extraneous routes for its production or destruction. N_2O generated from surfaces by laser irradiation could be one such source. N_2O made by unknown reactions when the laser was not tuned to the $O_2(A\text{-}X)$ transition is another.

The chosen analysis technique was infrared frequency-modulated diode laser absorption spectroscopy. The detection limit that we observed for our setup was 10 ppb. This limit was adequate for setting a low upper limit on the N_2O yield. In fact, only an upper limit could be derived; we did not see any N_2O produced that could be clearly identified with the $O_2(A) + N_2$ reaction.

RESULT HIGHLIGHTS

The Appendix contains a manuscript that was submitted to a special issue of *Faraday Transactions* devoted to atmospheric chemistry. We present here the most important findings from our work; the details are in the manuscript.

- 4:1 N_2/O_2 mixtures, purified to contain no N_2O, were irradiated for periods of several hours at wavelengths between 245 and 252 nm, corresponding to excitation to the $v = 7, 9$, and 10 levels in the $O_2(A^3\Sigma_u^+)$ state. An N_2O concentration of 5 ± 5 ppb was detected in unirradiated samples and a small additional amount of N_2O was detectable after irradiation. However, there was no significant difference in the amount of N_2O produced when the laser was on-resonance or off-resonance with lines in the $O_2(A^3\Sigma_u^+ \text{-} X^3\Sigma_g^-)$ bands. From these observations, we concluded that there is no evidence for the existence of an N_2O channel in the interaction of $O_2(A,v)$ with N_2, in spite of the fact that removal of these excited states by N_2 is very efficient.[5] The upper limit on the yield is set conservatively (i.e., the yield may be much lower, or zero) to 3×10^{-5}.

- Unknown chemistry could possibly cause N_2O that has formed to be subsequently destroyed. Prasad[6] suggests that the presence of ozone might be a key to such destruction, because of the variety of excited states that accompany its photodissociation in the 250-nm region. Ozone is definitely produced in the system, because we established that ozone is a product of the interaction of the $O_2(A)$ levels with O_2.[7] A demonstration that N_2O is stable under the conditions of the experiment is therefore essential. Experimental runs were made in which trace amounts of N_2O (40-90 ppb) were introduced into the system prior to irradiation. At the end of the run there had been no measurable loss of this N_2O, although ozone buildup was observed. From these observations, we conclude that, in our experiment, the concept that the $O_2(A)/N_2$ interaction *does* produce N_2O, which is destroyed during irradiation, is not valid.

- The question of the possible significance of a yield of 3×10^{-5} is addressed by comparing the corresponding production rate of N_2O with the modeled altitude-dependent loss rates. The peak $O_2(A)$ production occurs at ~45 km for an overhead sun.[8] At this altitude, the yield we have determined corresponds to a production rate of 3 molecules $cm^{-3}\ s^{-1}$, whereas the modeled loss rate is about 200 molecules $cm^{-3}\ s^{-1}$.[9] It follows that in the upper stratosphere, the $O_2(A) + N_2$ reaction provides at most a ~1% contribution to the N_2O production rate, a negligible quantity considering all the other uncertainties existing in our knowledge of N_2O sources and sinks. The process, if it takes place with a yield close to the upper limit that we established, could still affect the isotope ratios.

PUBLICATIONS AND PRESENTATIONS

The following publications were supported by this grant:

1. E. S. Hwang, B. Buijsse, R. A. Copeland, H. Riris, C. B. Carlisle, and T. G. Slanger, "Studies on the Generation of N_2O from Reaction of $O_2(A^3\Sigma_u^+)$ and N_2," *Faraday Transactions* (submitted, 1997).

The following presentations were or will be made on this project:

1. B. Buijsse, E. S. Hwang, T. G. Slanger, H. Riris, C. B. Carlisle, and R. A. Copeland, "Upper Limit for the Production of N_2O from the Reaction of $O_2(A^3\Sigma_u^+)$ with N_2," 1996 Fall Meeting of the American Geophysical Union, San Francisco, California, December 1996 [EOS, Trans. Amer. Geophys. Union **77**, No. 46, F534 (1996)].

2. R. A. Copeland, "Energy Transfer and Reactions of the O_2 Herzberg States Studied via Laser Techniques," 1996 Fall Meeting of the American Geophysical Union, San Francisco, California, December 1996 [EOS, Trans. Amer. Geophys. Union **77**, No. 46, F532 (1996)] (Invited presentation).

3. T. G. Slanger, E. S. Hwang, B. Buijsse, C. B. Carlisle, H. Riris, and R. A. Copeland, "Upper Limit for the Production of N_2O from the Reaction of Vibrationally Excited $O_2(A^3\Sigma_u^+)$ with N_2," 1997 Spring Meeting of the American Geophysical Union, Baltimore, Maryland, May 1997 (Invited presentation).

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APPENDIX

STUDIES ON THE GENERATION OF N_2O FROM REACTION OF $O_2(A^3\Sigma_u^+)$ AND N_2

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ABSTRACT

Evidence from several sources suggest possible *in situ* production of N_2O in the stratosphere. Considering that solar photoabsorption provides a large stratospheric source of $O_2(A^3\Sigma_u^+)$, and that vibrational levels of $v \geq 6$ are primarily removed by N_2, the $O_2(A^3\Sigma_u^+) + N_2$ system is studied to determine whether there is an atmospherically significant N_2O yield. Using 243-250 nm photoexcitation to produce vibrationally-excited $O_2(A^3\Sigma_u^+)$, and frequency-modulated diode laser spectroscopy as the detector of N_2O, we examine the products generated in a closed cell. We thereby set an upper limit of 0.003% on the N_2O yield for the process, and conclude that stratospheric N_2O production by this route is not significant compared to existing ground-based sources. The stability of N_2O in an $N_2O/O_3/N_2$ mixture subjected to prolonged 245 nm radiation is also studied. For low levels of O_3 and N_2O, no loss of N_2O is observed.

Submitted to Faraday Transactions (March 1997)

INTRODUCTION

N_2O is one of the more important molecules in the terrestrial atmosphere. Although present in quite small amounts, ~300 ppb throughout the troposphere,[1] it performs two very important functions. It is a greenhouse gas, in that it blocks infrared earthshine in spectral regions not blocked by other greenhouse gases, and it is a source of NO in the stratosphere, through the reactions

$$O_3 + h\nu \rightarrow O(^1D) + O_2(a^1\Delta_g) \qquad 1)$$

$$O(^1D) + N_2O \rightarrow NO + NO \qquad 2a)$$

$$\rightarrow N_2 + O_2. \qquad 2b)$$

The importance of reaction 2a is that NO consumes ozone,

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad 3)$$

and is then regenerated by the reactions

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad 4a)$$

$$NO_2 + O(^3P) \rightarrow NO + O_2. \qquad 4b)$$

These reactions constitute the NO_x catalytic cycle for ozone destruction. Thus, though itself unreactive with O_3, N_2O is instrumental in its control.

The N_2O concentration is slowly increasing throughout the atmosphere at the rate of about 0.2%/year because of biogenic/anthropogenic activity,[1] and as a result it is of great interest to make an inventory of N_2O sources and sinks. At present, there are major uncertainties in our knowledge, and a considerable range of estimates exists, although the trend is to conclude that known sinks are larger than known sources by some 30%.[1,2]

Considering that we live in an N_2/O_2 atmosphere, it has always been tempting to invoke the reaction

$$N_2 + O_2 \rightarrow N_2O + O \qquad 5)$$

as playing some atmospheric role. This reaction, making ground-state products, is 3.4 eV endothermic, which is equivalent in energy to a photon having a wavelength of 365 nm. As there is a great deal of solar radiation at this wavelength or shorter, it is logical to search for indirect pathways by which reaction 5 can be induced.

An obvious approach to this issue is to invoke internally excited reactants; there are many examples of reactions which do not occur with ground-state reactants, but occur readily when one of the reactants is excited. We may include the reaction of $N(^4S,^2D)$ atoms with O_2 , and $O(^1D,^3P)$ atoms with N_2O.

Recent experiments in this laboratory have established that the 4-5 eV electronically excited O_2 states can react with ground-state O_2 to make $O_3 + O$ with large yields,[3] and that collisional interactions between these excited O_2 states and N_2 are very rapid.[4-6] If this latter process takes place reactively, then only a very small yield of N_2O is required to make it atmospherically important.

Recent work showing that N_2O is isotopically fractionated in the stratosphere has considerable bearing on our understanding of atmospheric sources and sinks of this molecule.[7,8] Measurements show that tropospheric and stratospheric N_2O are isotopically distinct, implying that N_2O undergoes chemical changes during its atmospheric lifetime, currently estimated to be 90 years.[9] Such an effect could be due to isotopic exchange, since the principle stratospheric absorber, ozone, is isotopically fractionated,[10,11] but this observation is also consistent with the existence of an *in situ* N_2O source.

Prasad[2,12] presents numerous suggestions for N_2O sources and sinks, among them being collisions of electronically excited O_2 states with N_2, specifically $O_2(A^3\Sigma_u^+)$ and $O_2(B^3\Sigma_u^-)$, as well as collisions between "embryonic" O_3 and N_2. In the latter case, the reference is to nascent O_3 produced either in $O(^3P) + O_2$ or $O(^1D) + O_2$ collisions. These reactions are all conceivable N_2O sources and, to the extent that sources are required, bear investigation.

The idea of using electronically excited reactants to generate N_2O in the stratosphere (reaction 5) is not a new one, and 15 years ago there was a flurry of excitement over the work of Zipf[13] and Zipf and Prasad.[14] Zipf claimed that the reaction

$$N_2(A^3\Sigma_u^+) + O_2 \rightarrow N_2O + O \qquad 6)$$

had an N_2O yield of 60%, and Zipf and Prasad then showed that solar pumping of N_2 in the $N_2(A^3\Sigma_u^+ - X^3\Sigma_g^-)$ Vegard-Kaplan (VK) transition would lead to substantial amounts of N_2O production in the stratosphere and lower mesosphere. Although the absorption oscillator strength in the VK bands is very small, this property is offset by the density of N_2.

Over the next several years, experiments demonstrated that the yield of reaction 6 had been greatly overestimated. Black et al.[15] found a yield of less than 8%, Iannuzzi et al.[16] gave a yet smaller upper limit of 2%, and Fraser and Piper[17] found a value indistinguishable from zero. Therefore, this scheme has been laid to rest, although the problem with Zipf's experiment[13] has apparently not been explained.

Mechanistically, reaction 6 is not a very likely candidate for N_2O production, because generation of this molecule requires abstraction of an oxygen atom from O_2. The weakening of the N_2 bond, by excitation to $N_2(A)$, is less appropriate than if the opposite could be done, i.e., putting the initial excitation energy into the O_2 molecule and weakening the O-O bond,

$$O_2^* + N_2 \rightarrow N_2O + O. \qquad 7)$$

More direct N_2O production, by the recombination of N_2 and ground-state $O(^3P)$ in the atmosphere, does not occur, as it is spin-forbidden; ground-state N_2O asymptotically dissociates to $N_2 + O(^1D)$. However, when the labile O-atom is part of a triplet O_2 molecule, there is no restriction based on spin, and reaction 7 could take place if O_2^* has sufficient internal energy. Prasad[2] estimates the total energy to overcome the endothermicity and the activation barrier to be 107.4 kcal mole^{-1}, equivalent to 4.68 eV in the O_2^*. This energy corresponds to slightly less than the energy of the v = 4 level of the $O_2(A^3\Sigma_u^+)$ state.[18]

Of particular merit in considering excitation of the $O_2(A^3\Sigma_u^+)$ state as the starting point for N_2O production, as compared to the $N_2(A^3\Sigma_u^+)$ state, is that there is far more radiation available at 245-280 nm (the Herzberg state excitation wavelength range) than at the $N_2(A)$-pumping wavelength range, 180-200 nm. Moreover, the oscillator strength of the $O_2(A\text{-}X)$ transition is about an order of magnitude greater than that for $N_2(A\text{-}X)$.[19,20] Thus, the O_2^* process is potentially capable of producing N_2O much more copiously than the N_2^* process. We note that the Herzberg states are also produced higher in the atmosphere, in the 85-105 km airglow region, by O-atom recombination. Here too these states will be predominantly removed by N_2 collisions, and thus, any reactive yield is also pertinent at this altitude.

There are six known bound states of O_2 that dissociate to ground-state O-atoms: $A^3\Sigma_u^+$, $A'^3\Delta_u$, $c^1\Sigma_u^-$, $b^1\Sigma_g^+$, $a^1\Delta_g$, and $X^3\Sigma_g^-$.[18] These states are all metastable with respect to each other, and in the atmospheric regions of interest, up to 100 km altitude, collisional losses dominate radiative losses.[4,6,21,22] The $O_2(A^3\Sigma_u^+)$ state is the most rapid radiator, with a lifetime of 0.15 s,[23] and here we concentrate our studies on this state in levels $7 \leq v \leq 10$.

In previous considerations of reaction 7 as an N_2O source with $O_2(A)$ as O_2^*, a weak link has always been that there were various indications, going back to the 1960's, that N_2 might be an ineffective deactivator. In retrospect, these are not persuasive,[24,25] but the idea was made more explicit in the studies of Kenner and Ogryzlo,[26-28] who reported that O_2 was a more efficient collision partner for the lower vibrational levels of the Herzberg states than was N_2 by two orders of magnitude. These data muddied the waters and, in subsequent aeronomic calculations, the confusion was evident—sometimes N_2 was included as a collider, and sometimes not.

State-to-state experiments from this laboratory have now established that, contrary to being inert, N_2 is the *dominant* quencher of the high vibrational levels of the Herzberg states in the atmosphere. The most relevant measurements are the vibrational-level-specific studies of collisional removal rate constants for the Herzberg states by a variety of partners,[4,5,21] and the determination of ozone yields from the collision of $O_2(A)$ with O_2.[3] The latter bears considerable analogy with reaction 8a, the subject of this investigation.

$$O_2(A,A',c) + N_2 \rightarrow N_2O + O \qquad \text{8a)}$$

$$O_2(A,A',c) + O_2 \rightarrow O_3 + O \qquad \text{8b)}$$

In fact, all collision partners, including He and Ar, are effective at removing O_2 from the excited levels, and N_2 is generally at least half as fast as O_2 for the vibrational levels investigated. As the $[N_2]/[O_2]$ ratio in air is 4:1, it follows that removal by N_2 is the more important.

It is not evident *a priori* that reactions 8a and 8b will generate N_2O and O_3, respectively. Reaction 8a is endothermic by 3.4 eV, reaction 8b by 4.1 eV. However, for high vibrational levels of $O_2(A)$, reaction 8b is quite efficient, as ozone yields increase from ~ 0.1 for $v = 8$ to approximately unity for $v = 11$.[3] For reaction 8a to be an important atmospheric N_2O source, the necessary yields are minute compared to these figures.

EXPERIMENTAL APPROACH

The essence of the experiment is that static cells containing a mixture of O_2 and N_2 are photolyzed at wavelengths resonant with lines in absorption bands of the $O_2(A^3\Sigma_u^+ - X^3\Sigma_g^-)$ system and at similar wavelengths not resonant with O_2 absorption lines. Samples from these cells are then analyzed by frequency-modulated diode laser spectroscopy (FMS) for N_2O content. From the various physical parameters, an upper limit for the yield is then obtained for the fraction of deactivating $O_2(A^3\Sigma_u^+)/N_2$ collisions leading to N_2O production, when comparing on-resonance to off-resonance excitation. The experimental arrangement is shown in Figure 1.

Two identical cells arranged in series are used for long-term irradiation. This simultaneous irradiation confirms both the consistency of results and cell-to-cell variability. The cells contain O_2 and its collisional partner N_2. We excite a specific vibrational and rotational level of the $O_2(A^3\Sigma_u^+)$ state by pulsed laser excitation, and irradiate this closed system for a considerable period, typically 8 hours, allowing N_2O to rise to quantities adequate for analysis. Comparisons are made between on-resonance and off-resonance irradiation.

Before entering the double cell, the laser beam passes through another cell containing O_2 only. Here we keep the laser frequency in resonance with the chosen $A^3\Sigma_u^+$ transition by observing fluorescence from the v = 0 of the lower-lying $b^1\Sigma_g^+$ state. It has been demonstrated[29,30] that upon excitation of each of the Herzberg states, collisions with O_2 or N_2 result in population of the $O_2(b^1\Sigma_g^+)$ state. The $A^3\Sigma_u^+$ removal occurs rapidly at the operating pressure of 300 Torr, and a fraction of the $b^1\Sigma_g^+$ state molecules decays radiatively by emitting 762-nm light in the *b*-*X* 0-0 band. This radiation is the A ← X resonance signature. We note that the efficiency of the A → b process with O_2 as collider is not as high as originally stated by Bednarek et al.[29] The value has been decreased by approximately a factor of two.[31] Although the 762-nm signal is not strong, photon-counting for 20 s is sufficient to establish when the laser is on-resonance.

The laser system used for $O_2(A)$ excitation is an excimer-pumped dye laser operating with Coumarin 503 dye. The 488-504 nm output is frequency doubled (BBO) to get the desired wavelength of 244-252 nm. The pulse energy is 300-500 μJ at a repetition frequency of 10 Hz. This radiation is used to excite the F_2 fine-structure components of both the $^{Q}P_{21}$ and $^{Q}R_{23}$ N = 5 transitions in the 9-0 and 10-0 bands of the A-X transition, and the N = 7 pair in the 7-0 band.[32] These two components overlap within the bandwidth of the laser (~ 0.35 cm^{-1}) and can be considered as one strong transition with a slightly adjusted linewidth.

The gas handling system incorporates molecular sieve 5A traps for removal of the N_2O impurity from the O_2 and N_2 gas cylinders. N_2O was invariably present and this treatment brought the levels down to the detection limit. The stated purity of O_2 in these experiments is 99.995%, and that of N_2 is 99.99%. The cells are pumped down to a pressure of 10 mTorr with a mechanical vacuum pump prior to filling.

During the long-term irradiation of the closed cells, O_2 flows through the resonance cell at a flow rate of 175 $cm^3\ s^{-1}$ and a pressure of 300 Torr. Flowing the O_2 removes another 762-nm radiation source – ozone. O_3 builds up quite rapidly in the static system, being formed in the collision of $O_2(A^3\Sigma_u^+)$ with ground-state O_2 (reaction 8b).[3] Dissociation of O_3 in the Hartley band forms $O(^1D)$ atoms which, in collision with ground-state O_2, result in the formation of $O_2(b^1\Sigma_g^+)$ with a quantum efficiency of ~70%.[22] This process can therefore contribute to the 762-nm signal. Once O_3 is generated in the cell, the 762-nm signal becomes independent of the excitation wavelength, as the Hartley band is very broad.

The resonance cell is a single pass cell, with a plane entrance window, and a Brewster's angle exit window to reduce scattered light. A fused silica lens (50-cm focal length) focuses the light in the center of the cell. Connected to the cell is a photomultiplier tube (PMT) shielded with two Wratten 89B long pass filters to block UV radiation. Photon counting is used to monitor the relatively long-lived (~200 μs) 762-nm signal.

The reaction cells contain 20% O_2 and 80% N_2 at a total pressure of 700 Torr, and are connected together by an internal plane window separating the two gas volumes. This procedure is used to check the consistency of the measurements. The cells have external plane windows and are positioned in an eight-pass cavity, the length of each cell being 15.2 cm. The incoming beam has an intensity of 400 μJ, which is reduced to 40 μJ after the eight passes through the pair of cells and uncoated quartz windows. The relative intensity of the outgoing beam is monitored with a photodiode and also stored in the computer during the irradiation.

When an irradiation run is complete, samples are transferred into a multipass cell having a 10-meter path length, and analyzed for N_2O using the sensitive FMS technique.[33,34] Calibration is carried out by introducing the same pressure of air, 2.5 Torr, into the FMS cell, and measuring the shape and intensity of the 300 ppb reference signal. By a linear least squares fit, the sample signal is compared to the reference signal. Room air is remeasured at the end of the analysis to account for any signal drift with time; agreement is typically within ±10%. The ultimate detection sensitivity is determined by the noise level on a particular day, and the N_2O produced due to the irradiation is in principle determined by the increment over the non-irradiated cell.

The FMS uses a diode laser source, tuned to one of the strong N_2O absorption lines in the ν_3 band near 2234 cm^{-1}. The laser is injection-modulated at radio frequencies (RF), and as a result, the output optical beam from the laser is frequency-modulated at the applied RF. If this laser beam is directed through a sample cell containing an absorbing gas, the resulting absorption converts some of the laser frequency modulation (FM) into amplitude modulation (AM). This AM signal can easily be detected using a photodiode of suitable bandwidth and appropriate RF signal processing electronics. The advantage gained by the

RF modulation and detection is that the signal of interest occurs in a frequency regime where the laser has very low noise, and quantum-limited detection sensitivity is possible. In the weak modulation limit, the power spectrum of the output beam consists of a strong carrier component at the natural emission frequency of the diode laser, and weaker upper and lower sidebands displaced from the carrier by the applied RF.

When this light impinges on a photodetector, each sideband mixes with the carrier to give a signal at the modulation frequency. One important property of the FM light is that the upper and lower sidebands are equal in amplitude, but opposite in phase, so that the two signals generated by the mixing process cancel exactly. If, prior to the detection process, something changes the relative amplitudes or phases of the sidebands, then this perfect cancellation no longer occurs. The result is a detector photocurrent at the modulation frequency, as illustrated in Figure 2. In a trace gas detection application, this condition is obtained by adjusting the laser emission and modulation frequencies so that a strong absorption line of the molecular species of interest is coincident with one of the sidebands.

One practical difficulty in the application of FMS to the detection of pressure-broadened absorption features is the requirement that photodiodes have bandwidths comparable to the modulation frequencies used. Generally, high-bandwidth photodetectors are expensive and have small, highly damage- and alignment-sensitive active areas, which makes them difficult to use in a practical field instrument. A variation of FMS, two-tone FMS, is used in the present case, and provides a convenient solution to these problems.[35,36] In two-tone FMS, the diode laser is modulated simultaneously at two radio frequencies, ω_1 and ω_2, which are offset from each other by a conveniently chosen intermediate frequency Ω. The principles and high-sensitivity features of two-tone FMS are similar to those of conventional FMS, but the detection of the signal takes place at the frequency Ω, which is generally chosen to be high enough to lie in a low-noise region of the laser intensity noise spectrum, but low enough to allow the use of inexpensive, large area, intermediate-bandwidth detectors. Typical intermediate frequencies are in the 1-10 MHz range.

RESULTS AND DISCUSSION

N_2O Production

The data are presented graphically in Figure 2 and summarized in Table 1. In Figure 2, panel a), we show the large N_2O signal associated with the 300 ppb mole fraction in room air. Panel b) shows the lack of a significant signal from an un-irradiated N_2/O_2 sample mixture, when each gas has been stripped of any N_2O. Panels c) and d) show the N_2O signals from irradiated samples, which are rather similar irrespective of whether irradiation occurred on-resonance with an $O_2(A\text{-}X)$ line, or off-resonance.

Table 1 shows the data for N_2O production for the three different $O_2(A)$ vibrational levels investigated. We first note that the background level, is 5 ± 5 ppb, from 23 measurements on un-irradiated cells. There are four columns for the on-resonance signals. The first gives the absolute amount of N_2O measured, while the second gives the total number of photons that have passed through the cells (the absorbing gas, O_2, has a constant partial pressure). Since there is very little N_2O found in the absence of irradiation, we make the assumption that N_2O appearance, whatever its source, is linear in photon flux. Thus, we wish to compare averages of N_2O produced per photon absorbed, so we initially subtract 5 ppb for each value in the N_2O column. The third column is the ratio of the modified first column and the photon flux. In the fourth column, we calculate the N_2O yield based on the parameters described below.

Yield Calculations

As accurate measurements are critical, we illustrate the yield determinations by carrying out a set of calculations based on excitation to the v = 9 level of the $A^3\Sigma_u^+$ state. The integrated cross section for absorption via the relatively strong closely-spaced $^QR_{23}$ + $^QP_{21}$ (N = 5) line pair is (6.84 ± 0.13) × 10^{-24} cm^2 cm^{-1}.[37] The maximum cross section σ can be calculated from the linewidth, $\Delta\nu_{abs}$, of the transition. Yoshino et al.[37] give a Doppler linewidth of (0.086 ± 0.001) cm^{-1} for lines in the *A*-*X* 9-0 band at zero pressure and 300 K, and measured a pressure dependence of (8.6 ± 0.1) × 10^{-5} cm^{-1} $Torr^{-1}$. A pressure of 700 Torr broadens the lines to (0.146 ± 0.001) cm^{-1}. The cross section σ is the integrated cross section divided by $(\pi/4\ln2)^{1/2}\Delta\nu_{abs}$. This results in a cross section σ for the excited line of 3.79 × 10^{-23} cm^2.

The laser linewidth, $\Delta\nu_{laser}$, had been previously determined by scanning the laser over four different rotational transitions in the v = 9 band at 4.8 Torr and room temperature. We fit the observed transitions with Gaussians and found linewidths of (0.25 ± 0.03) cm^{-1}. These lines are however a convolution of both laser linewidth and absorption linewidth: the proper linewidth $\Delta\nu_{laser}$ is $((0.25)^2 - (0.09)^2)^{-}$ = (0.23 ± 0.03) cm^{-1}. When the laser has maximum overlap with the transition pair the fractional absorption γ is

$$\gamma = \frac{1}{\sqrt{1+\left(\frac{\Delta\nu_{laser}}{\Delta\nu_{abs}}\right)^2}} \qquad (9)$$

which has a value of (0.46 ± 0.05). The number of O_2 molecules excited via the line pair is N_A:

$$N_A = \gamma N\sigma[O_2]\mathrm{ln}_1\, n_2 \qquad (10)$$

where N is the number of photons in each laser pulse. With a laser power of 190 μJ per pulse at a wavelength of 246.46 nm, N is 2.35×10^{14} photons. Absorption takes place over a total length $l = 15.2$ cm, and $[O_2]$ is the oxygen concentration, $4.6 \times 10^{18}\ cm^{-3}$ at a partial pressure of 140 Torr. The number of passes, n_1, is eight, and n_2 is the number of laser pulses in the total irradiation time. After 420 minutes of irradiation with a 10 Hz laser, n_2 is 2.52×10^5. This leads to a value for N_A of 5.7×10^{17}.

With added N_2, the $O_2(A^3\Sigma_u^+)$ molecules will be quenched by both O_2 and N_2. The partial pressures determine the fraction that will be quenched by N_2. This fraction is given by

$$\beta = \frac{k_{N_2}[N_2]}{\left(k_{O_2}[O_2] + k_{N_2}[N_2] + k_{rad}\right)} \tag{11}$$

Knutsen et al.[4] measured rate constants for collisional removal of $O_2(A^3\Sigma_u^+)$ for several gases, finding values for k_{O_2} of $(5.7 \pm 0.4) \times 10^{-11}\ cm^3\ s^{-1}$ and k_{N_2} of $(4.3 \pm 0.3) \times 10^{-11}\ cm^3\ s^{-1}$; the contribution of k_{rad}, the radiative decay, is negligible. At partial pressures of 560 Torr N_2 and 140 Torr O_2, β is 0.75 ± 0.07.

The N_2O yield ε for the removal of $O_2(A^3\Sigma_u^+)$ by N_2 can be calculated from the concentration of N_2O in the sample after irradiation. This yield is given by:

$$\varepsilon = \frac{V[N_2O]}{N_A \beta} \tag{12}$$

where V is the volume of the cell, 81 cm^3. The N_2O concentration is the observable of the experiment, measured by FMS.

The yields appear in the fourth column of the on-resonance data in Table 1. For the three vibrational levels, they lie in the range of $(1\text{-}5) \times 10^{-5}$. Taking the average value, 3×10^{-5}, as a typical yield is very conservative, since this does not take into account that the on- and off-resonance signal averages are essentially the same, at least for $v = 7$ and 9. Thus, the data in Table 1 do not unambiguously support *any* N_2O yield from gas-phase chemistry that is different from zero. Nevertheless, it is appropriate to give an upper limit, and we believe 3×10^{-5} to be a generous one. As discussed below, this figure is much smaller than that needed for $O_2(A^3\Sigma_u^+) + N_2$ to be a significant N_2O source. For $v = 10$, we see that the on-resonance average is almost twice as large as that for off-resonance. However, the scatter in individual runs is large enough that a more statistically meaningful study would be needed to determine if indeed there is a small yield associated with the $v = 10$ level. Of course, if only $v \geq 10$ excitation leads to N_2O production, it will be a rather ineffective source. The topmost $O_2(A)$ level is $v = 12$, which has recently been found to be very weakly bound.[38]

The off-resonance N_2O source is a matter of some interest and the obvious explanation is wall desorption. As the laser is multi-passed in the cell, the walls and windows are being scoured, and it is not surprising to detect N_2O. In previous work in this laboratory, using rare-gas resonance-lamp sources, experiment showed that CO was copiously produced by irradiation of an empty cell, which was interpreted as dissociation of CO_2 adsorbed on the walls.[39]

A gas-phase reaction that might conceivably make N_2O is that between electronically or vibrationally excited O_3 with N_2, where the source of the former would be $O + O_2$ recombination, and the O-atom source is O_3 photodissociation. This reaction has been discussed by Prasad,[2,12] but it probably has no role in our off-resonance experiments because no ozone build-up was observed under those conditions in spite of the generation of N_2O.

Observation of Ozone Build-up

A question that arises in the course of these experiments concerns the possible role of the ozone build-up on N_2O destruction. Prasad has suggested[12] that the presence of ozone may lead to loss of N_2O in experiments of this type, leading to incorrect conclusions regarding N_2O yields. To address this potential complication, we measured the extent of O_3 build-up during irradiation, and also determined whether an N_2O loss could be observed following deliberate introduction of low levels of N_2O prior to irradiation.

Measurement of ozone production are made in the multipass reaction cell, where an energy meter is used to detect the increased UV absorption as ozone builds up. We make a Beer's law calculation of the amount of ozone produced in a given time for the three different $O_2(A)$ vibrational levels that were investigated. This can then be compared with an earlier study,[3] where the yield of oxygen atoms produced by reaction 8b, for v = 9-11, was determined. An ozone build-up curve is shown in Figure 3. Ozone amounts were measured for 2100 s irradiation times for an O_2 pressure of 700 Torr, and 1-10 ppm O_3 was observed, dependent on the initial $O_2(A)$ vibrational level. Adjusting for the different oscillator strengths for the *A-X* 7-0, 9-0, and 10-0 bands,[19,37,40] the O_3 yield ratios are 0.17:0.39:1.0 for v = 7, 9, and 10. Copeland et al.[3] reported ratios of 0.52(±0.18):1.0 for v = 9 and 10.

The stability of N_2O in the presence of O_3 is important to determine, because if it is unstable, it would adversely affect our measurements. In a study made several years ago in this laboratory,[15] in a mixture of O_3, N_2O, and N_2 irradiated by light from a 254-nm mercury lamp, the N_2O concentration fell significantly after 15 minutes. However, in the present study, both O_3 and N_2O are present at much lower concentrations than in the previous case. Both studies were made at a pressure close to one atmosphere, but in the earlier work the O_3 pressure was 1 Torr, compared to up to 0.007 Torr in the present case, while the earlier N_2O concentration was 20-200 mTorr, compared to the present concentration of 0.03-0.06 mTorr.

The new measurements are made by introducing N_2O (but not O_3) into the N_2/O_2 mixture, then irradiating for six hours on the $O_2(A)$ v = 9 level, leading to a build-up of ozone to 0.004 Torr. Upon analysis, we find no discernible change in the N_2O concentration. Since O_3 or its photodissociation products were implicated in the former study as the ultimate cause of the N_2O loss,[15] the much lower O_3 densities used here are probably relevant to the observation.

Atmospheric Significance

Any proposed new source of N_2O must be tested against pre-existing sources to establish if its inclusion will make a substantial difference to the models. In order to evaluate the importance of reaction 8a in atmospheric chemistry, modeling calculations are required, and fortunately we can avail ourselves of previous efforts in this direction.

The $O_2(A^3\Sigma_u^+)$ production rate in the atmosphere from solar photoabsorption is proportional to the O_2 density down to the altitude where the atmospheric transmittance is reduced by ozone photoabsorption at 245-280 nm. As a result, $O_2(A)$ production peaks at 45 km, and then falls sharply, with little production below 35 km.

The peak production for all vibrational levels is 1.5×10^5 cm^{-3} s^{-1}, which can be determined from the photoabsorption rate coefficients for individual $O_2(A\text{-}X)$ bands, calculated by Shi and Barker,[41] the O_2 altitude profile, and an ozone transmittance function. About 75% of the $O_2(A)$ is quenched by N_2 for $A^3\Sigma_u^+$ state vibrational levels v = 6-11, and in fact the higher levels are more important than the lower, both because of increasing Franck-Condon factors and because the lower levels are less likely to be reactive. Shi and Barker find that the v = 6-11 vibrational levels account for 72% of the photoproduction rate of

$O_2(A)$. Including all the $A^3\Sigma_u^+$ levels, and using a yield for the reactive channel of 3×10^{-5}, we arrive at an upper limit on the N_2O production rate of 3 cm^{-3} s^{-1}.

Comparison can then be made with the N_2O loss rate at this altitude. Minschwaner et al.[42] have used line-by-line calculations for absorption by the Schumann-Runge system of O_2 to determine the transmittance of the atmosphere to radiation that will dissociate N_2O, primarily at 190-210 nm. At 43 km, they calculate that the diurnally averaged N_2O loss rate due both to photodissociation and to reaction with $O(^1D)$ is approximately 200 cm^{-3} s^{-1}, for a latitude range of 0-40 degrees. For 50 km, Prasad[2] gives a value of 90 cm^{-3} s^{-1}. Therefore, the upper limit to the N_2O production rate that we have determined corresponds to approximately 2% of the loss rate at the peak of the $O_2(A)$ production profile.

At higher altitudes the $O_2(A)$ excitation rate decreases with the O_2 density, but the N_2O density decreases far more rapidly, as the mixing ratio falls as well as the total air density.[8] As a result, the contribution made by the $O_2(A)$ + N_2 reaction to the fractional N_2O production rate could become substantially larger than 2%. Nevertheless, at the altitudes of primary interest, below 50 km, the contribution of this reaction to the global N_2O budget is minor, and is completely overshadowed by other sources and their uncertainties.

Finally, we should point out that any reactive channel that makes N_2O could be isotope-specific. Even a small fractional production of N_2O might over time result in isotopic fractionation, given the extremely long lifetime of N_2O in the atmosphere.

CONCLUSIONS

$O_2(A^3\Sigma_u^+)$ is produced in substantial amounts from O_2 in the upper stratosphere by solar photoabsorption. We have investigated whether the predominant fate of these molecules, collisional removal by N_2, leads with some atmospherically significant yield to N_2O. The measurements have been performed on the v = 7, 9, 10 levels of $O_2(A)$, and the results have been negative, with a conservative upper limit for the reaction yield of 3×10^{-5}. In contrast, the analogous interaction with O_2 as the collider leads to large yields of O_3.

Another issue that we have addressed is the stability of N_2O in the presence of O_3 in an N_2 bath during 245 nm irradiation. Earlier results from this laboratory indicated that N_2O became depleted in such a system, but the new measurements at much lower concentrations of both N_2O and O_3 show no such effect. Thus, the absence of a significant N_2O yield from $O_2(A^3\Sigma_u^+) + N_2$ is a consequence of lack of production, and not of subsequent destruction.

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FIGURE CAPTIONS

Figure 1. Schematic apparatus diagram.

Figure 2. Frequency modulated N_2O signal as a function of infrared diode laser wavelength. N_2O signal in room air is shown in panel a) and the magnitude is used as the 300 ppb standard. N_2O signals from un-irradiated O_2/N_2, and from O_2/N_2 irradiated off-resonance and on-resonance with lines in the O_2 (*A*-*X*) 10-0 band state are displayed in panel b), c), and d), respectively. It can be seen that the N_2O signal in the un-irradiated cell is in the noise level (~ 5 ppb), while a clear N_2O signal is observable in the off- and on-resonance irradiated cells (~ 15 ppb).

Figure 3. Ozone absorption determination. The top curve represents the laser intensity before the cell to monitor energy fluctuations during the measurement. The bottom curve is the intensity after the cell. The gas in the reaction cell was pumped out at the end of the measurement (around 3000 s, shown as a sharp rise in the absorption curve). The amount of ozone in the cell was estimated from a Beer's law calculation (see the text).

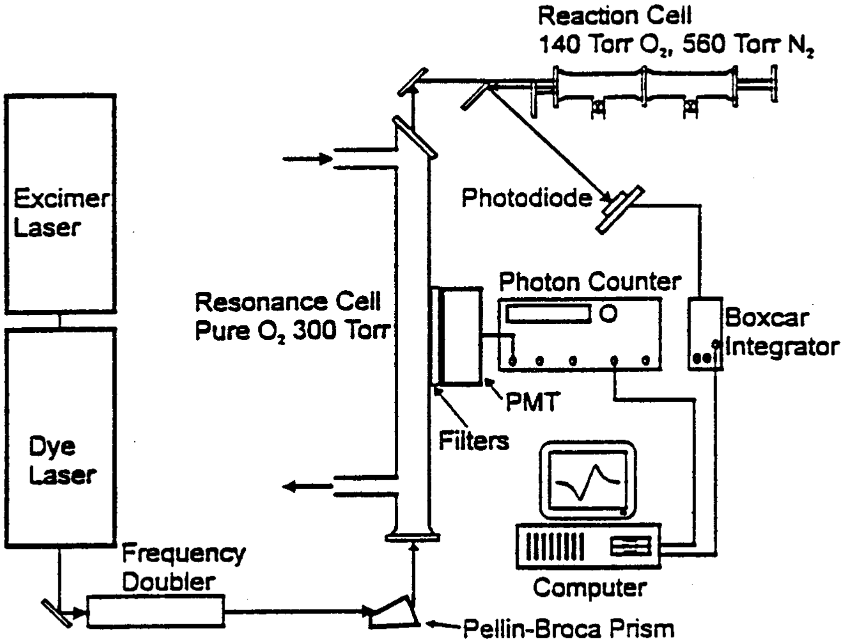
Reaction Cell
140 Torr O_2, 560 Torr N_2
Excimer Laser
Dye Laser
Photodiode
Photon Counter
Boxcar Integrator
Resonance Cell
Pure O_2 300 Torr
PMT
Filters
Computer
Frequency Doubler
Pellin-Broca Prism

Figure 1

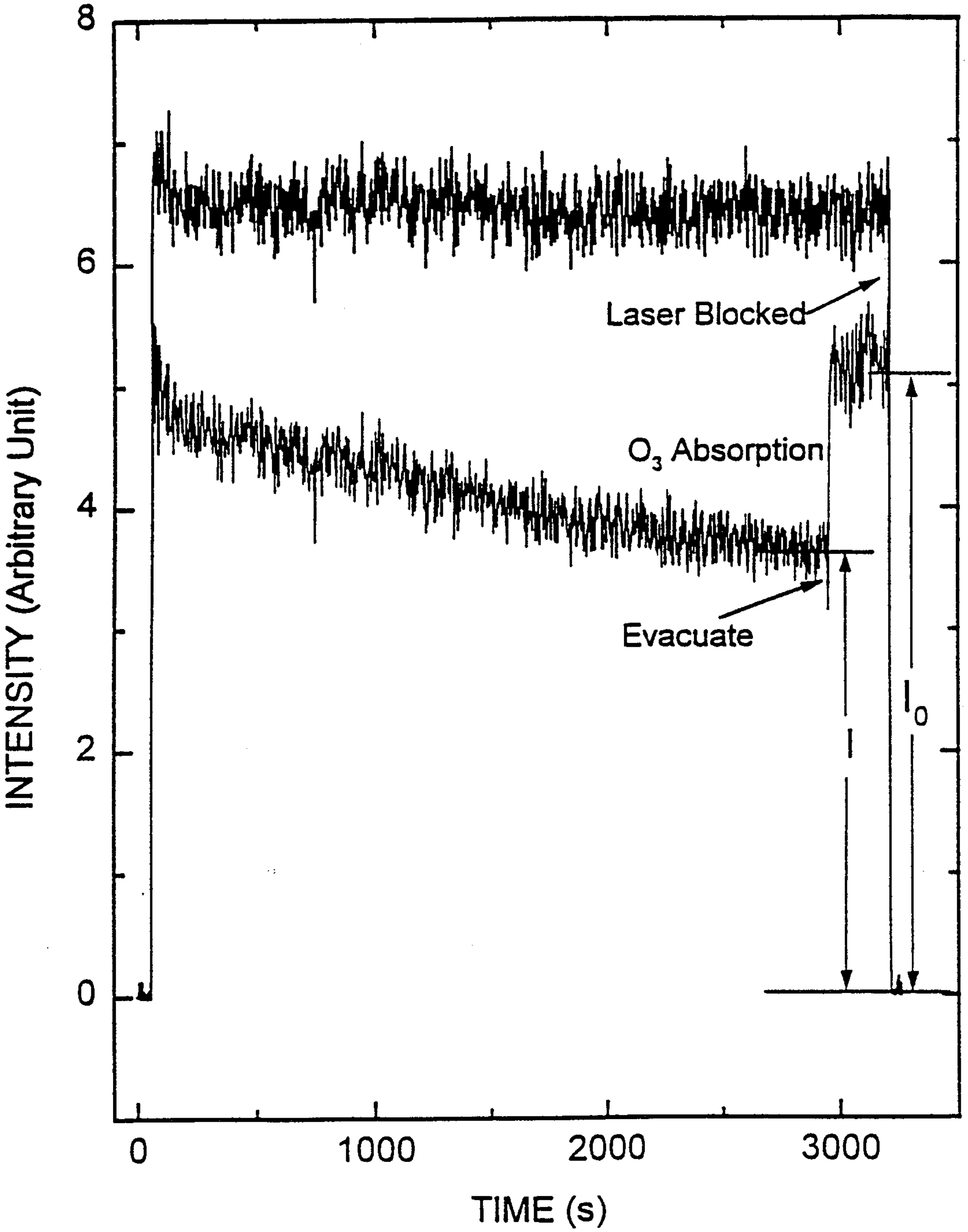
INTENSITY (Arbitrary Unit)
TIME (s)
0
1000
2000
3000
0
2
4
6
8
Laser Blocked
O_3 Absorption
Evacuate
I
I_0

Figure 2.

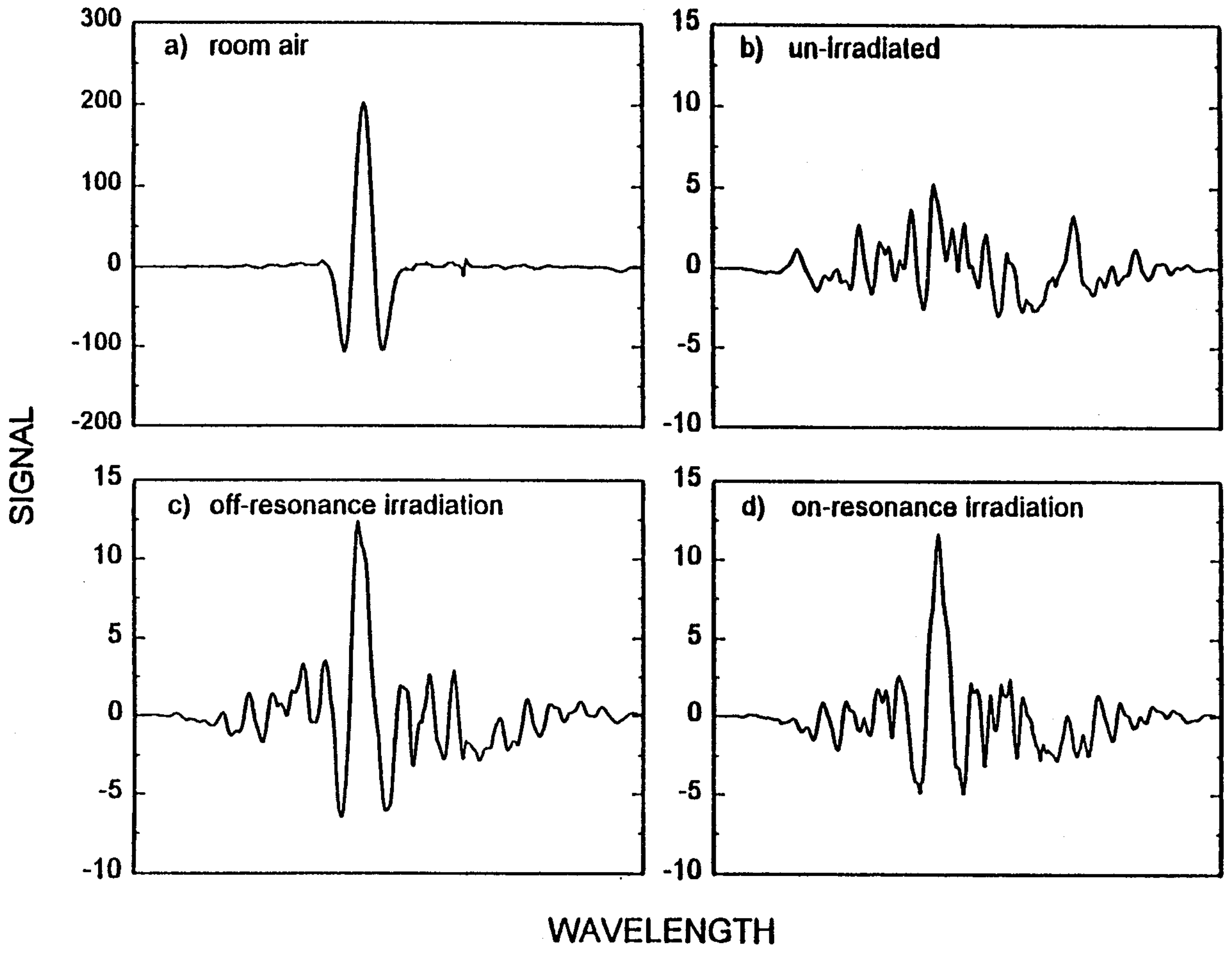
300
200
100
0
-100
-200
a) room air
15
10
5
0
-5
-10
b) un-irradiated
15
10
5
0
-5
-10
c) off-resonance irradiation
15
10
5
0
-5
-10
d) on-resonance irradiation
SIGNAL
WAVELENGTH

Figure 3

Table 1. N_2O concentration in the reaction cell following irradiation both on and off-resonance with O_2 ($A^3\Sigma$, υ) transition.

vibrational level	on-resonance irradiation				off-resonance irradiation		
	N_2O (ppb)[a,b]	photons ($x10^{20}$)	N_2O[c]	yield (ε) ($x10^{-5}$)	N_2O (ppb)[a,b]	photons ($x10^{20}$)	N_2O[c]
7	18	12	1.1	2.3	14	11	0.8
	10	12	0.4	0.9	13	11	0.7
		average	0.8	1.6 ± 1.1			0.8
9	17	8	1.5	2.5	15	8	1.3
	19	8	1.8	2.7	19	8	1.8
	10	4	1.3	1.9	2	3	0.0
	17	4	3.0	4.7	12	3	2.3
	15	13	0.8	1.2	42	13	2.8
	7	13	0.2	2.5	22	13	1.3
		average	1.4	2.6 ± 1.2			1.6
10	26	9	2.3	3.9	13	7	1.1
	18	9	1.4	2.4	8	7	0.4
	13	6	1.3	2.1	17	7	1.7
	8	6	0.5	0.8	6	7	0.1
		average	1.4	2.3 ± 1.3			0.8

[a] Background N_2O concentration in the un-irradiated cell is 5 ± 5 ppb.

[b] By comparison to N_2O in room air as standard (300 ppb).

[c] Normalized for N_2O concentration per 10^{20} photons following subtraction of the background (5 ppb).