MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1961-A
Spectroscopic Parameters for Ozone From Infrared and Ultraviolet Techniques

S.M. ADLER-GOLDEN
R.A. ARMSTRONG

12 August 1982

Approved for public release; distribution unlimited.

OPTICAL PHYSICS DIVISION
AIR FORCE GEOPHYSICS LABORATORY
HANSCOM AFB, MASSACHUSETTS 01731

AIR FORCE SYSTEMS COMMAND, USAF
This report has been reviewed by the ESD Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS).

This technical report has been reviewed and is approved for publication.

DR. ALVA T. STAIR, JR.
Chief Scientist

Qualified requestors may obtain additional copies from the Defense Technical Information Center. All others should apply to the National Technical Information Service.
SPECTROSCOPIC PARAMETERS FOR OZONE FROM INFRARED AND ULTRAVIOLET TECHNIQUES

S. M. Adler-Golden
R. A. Armstrong

Air Force Geophysics Laboratory (OPR-1)
Hanscom AFB
Massachusetts 01731

Air Force Geophysics Laboratory (OPR-1)
Hanscom AFB
Massachusetts 01731

Approved for public release; distribution unlimited.

The spectral contribution of ozone in the upper atmosphere is a function of the vibrational levels populated in the formation reaction and the time-dependent behavior of those levels. A qualitative analysis of the spectroscopic and Einstein coefficients behavior based on infrared and ultraviolet techniques is presented.
Contents

1. INTRODUCTION .......................... 5
2. CALCULATIONS OF VIBRATIONAL LEVELS FOR OZONE 6
3. EINSTEIN COEFFICIENTS FOR OZONE 9
4. ULTRAVIOLET INVESTIGATIONS OF OZONE 13
REFERENCES ............................. 21

Illustrations

1. Ozone Transition Energies and Relative Boltzmann Populations 10
2. Relative Vibrational Intensities for Emitting Levels Using (a) Unperturbed Harmonic Oscillator and (b) Harmonic Oscillator Perturbed by Darling-Dennison Resonance 12
3. Ultraviolet Absorption Spectrum of Ground State Ozone 15
4. Calculated Ultraviolet Absorption Spectrum of Vibrationally Excited Ozone, $1\nu_1$, and $1\nu_3$ 16
5. Ultraviolet Absorption Spectrum of Vibrationally Excited Ozone, $e^o$ 17
6. (Red Shift)/(Change in $\sigma^2$) vs Time After Photolysis of a 0.02 Torr $O_3/115$ Torr $O_2$ Mixture 18
Tables

1. Ozone Energy Levels .............................................. 8
2. (Matrix Element) $\times 2$ for $\Delta v_3 = -1$ Transitions ...... 11
3. $(\Delta v_3 = -3, \Delta v_2 = 2)$ Transitions ................. 12
Spectroscopic Parameters for Ozone From Infrared and Ultraviolet Techniques

1. INTRODUCTION

Ozone is an important source of infrared background radiation in the upper atmosphere. The spectral extent of this ozone emission is a function of the distribution of emitting vibrational levels. In the 80- to 120-km altitude region, high vibrational levels are populated via the $O + O_2 + M \rightarrow O_3^* + M$ recombination reaction, and it appears that a significant portion of these levels can emit prior to collisional relaxation. Thus, information concerning the population and relaxation of excited vibrational levels of ozone in the atmosphere is highly valuable.

Several approaches are currently under way to obtain information on the ozone recombination. One is the direct measurement of atmospheric IR radiance using rocket-borne probes. Unfortunately, this approach is costly, and alternatives involving laboratory rather than field experiments are thus very appealing. The most sophisticated laboratory approach currently available utilizes the COCHISE

(Received for publication 11 August 1982)

(Cold Chemi-excited Infrared Simulation Experiment) apparatus at the Air Force Geophysics Laboratory (AFGL). Ozone is formed under low pressure conditions similar to the upper atmosphere; the resulting chemiluminescence is measured in a cryogenic environment that enables high sensitivity and good spectral resolution. The $\nu_3$ band emission has been investigated. Hot band emission has been observed, but the nascent distribution has not been directly measured, and its derivation must rely on estimated Einstein "A" coefficients for $\nu_3 > 1$.

Another method of obtaining information about the ozone recombination is based on time-resolved ultraviolet absorption measurements of ozone formed following pulsed excitation of oxygen or ozone-oxygen mixtures. Bair and co-workers have obtained extensive data in a system in which high pressures (about 0.1 to 1 atm) of O$_2$ to O$_3$ mixtures are flash-photolyzed, and the resultant O atoms recombine on a time scale of tens of microseconds. In these experiments the UV Hartley band of the freshly-formed ozone is seen to be altered from its normal appearance. Early workers attributed this effect to ozone being formed in a "precursor" state of an unspecified nature, which subsequently relaxes to ground-state ozone. Recent work has identified the precursor as vibrationally excited ozone. Bair and co-workers have indeed attempted to extract vibrational distributions and relaxation rates from their data. Although their spectral analysis method is not exact, their work demonstrates that quantitative information on the recombination can be extracted from UV spectra. A more careful analysis is definitely required.

This report is a result of our investigation of the ozone data base and consequent analysis of approaches to understanding atmospheric nonequilibrium radiative properties of ozone. The first two sections, the energy levels and Einstein "A" coefficients, are directly applicable to analysis of AFGL field and COCHISE results. The last section, an ultraviolet diagnostic for ozone, exemplifies an alternative approach that will supplement the analysis.

2. CALCULATIONS OF VIBRATIONAL LEVELS FOR OZONE

Chemiluminescence from high vibrationally-excited states of ozone resulting from the reaction O + O$_2$ + M $\rightarrow$ O$_3^+$ + M has been observed in COCHISE. A full analysis of the signal requires knowledge of the emission frequencies, $\nu$, given by

$$h\nu = E(v_1, v_2, v_3) - E(v_1, v_2, v_3 - 1)$$

(Due to the large number of references cited above, they will not be listed here. See References, page 21.)
as well as the Einstein coefficients (inverse lifetimes), denoted
A(v_1, v_2, v_3)→(v_1', v_2', v_3'-1), for all vibrational levels (v_1', v_2', v_3') that are
appreciably populated in the ozone forming reaction.

The most extensive tabulation of energy levels E(v_1, v_2, v_3) is found in
Barbe. All levels having up to 3 quanta, (that is, v_1 + v_2 + v_3 ≤ 3) are
included. In addition, several 4-quantum levels are observed. Most of
the data is derived from absorption measurements using a long optical pass
(l × c = 2.5 meter-atm) in a double beam spectrometer. The results are
summarized in Table 1 in the "Exptal." column.

Spectroscopic constants for the energy levels were determined by the following
procedure. First the formula

\[ E_u = \sum_{i=1}^{3} \omega_i (v_i + \frac{1}{2}) + \sum_{i,j=1}^{3} x_{ij} (v_i + \frac{1}{2}) (v_j + \frac{1}{2}) \]  

(2)

is used to find E_u, the energies of (hypothetical) unperturbed levels. Then a
Darling-Dennison perturbation is added which couples the stretching motions and
alters these levels. The resulting perturbed levels are obtained by diagonalizing
the perturbation matrix. The appropriate matrix elements in the harmonic
oscillator basis are given explicitly in Reference 6. (The matrix diagonalization
is very straightforward, especially since for v_1 + v_3 ≤ 5 it is at most a 3 × 3.)
The perturbed levels calculated by Barbe according to this prescription appear in
Table 1 in the "Barbe Calc." column. Agreement with the experimental energy
values is excellent, typically better than 1 cm⁻¹.

Clearly, the foregoing method for finding the energy levels can be extended to
include those levels not already tabulated. We have performed the calculation on
levels relevant to the COCHISE experiment for up to 5 quanta. The results are pre-
sented in Table 1 under "Current." To check the accuracy of the current work, the
values may be compared with the "Barbe Calc." column. There are some minor
discrepancies between the two columns, the source of which is unclear, but gener-
ally the agreement is good. It appears that the 4-quantum levels should agree with
experiment to within about 1 cm⁻¹. The 5-quantum levels may be somewhat less
accurate. Calculations on higher v-levels are not shown as it may be unrealistic to
expect accurate results at such high energies. In fact, 5- and 6-quantum levels
may lie in the quasi-continuum.

Darling and Dennison resonance and anharmonic potential function of

molecules II. Application to O₃: Laser-Induced Processes in Molecules
(K. L. Kompa and S.D. Smith, Ed.), Springer Series in Chemical Physics,
Table 1. Ozone Energy Levels (cm⁻¹)

<table>
<thead>
<tr>
<th>Level</th>
<th>Exptal.</th>
<th>Barbe Calc.</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1103.15</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>010</td>
<td>700.93</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>*001</td>
<td>1042.096</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>200</td>
<td>2201.3</td>
<td>2201.6</td>
<td>2201.8</td>
</tr>
<tr>
<td>020</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>*002</td>
<td>2058.0</td>
<td>2057.8</td>
<td>2057.7</td>
</tr>
<tr>
<td>*101</td>
<td>2110.79</td>
<td>2110.5</td>
<td>…</td>
</tr>
<tr>
<td>*110</td>
<td>1795.3</td>
<td>1795.0</td>
<td>…</td>
</tr>
<tr>
<td>*011</td>
<td>1726.4</td>
<td>1726.0</td>
<td>…</td>
</tr>
<tr>
<td>300</td>
<td>…</td>
<td>3291.3</td>
<td>3291.3</td>
</tr>
<tr>
<td>030</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>*003</td>
<td>3046.0</td>
<td>3045.2</td>
<td>3045.0</td>
</tr>
<tr>
<td>210</td>
<td>…</td>
<td>2884.2</td>
<td>2884.0</td>
</tr>
<tr>
<td>201</td>
<td>3185.7</td>
<td>3186.5</td>
<td>3186.7</td>
</tr>
<tr>
<td>120</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>021</td>
<td>2409.5</td>
<td>2408.0</td>
<td>…</td>
</tr>
<tr>
<td>*102</td>
<td>3084.1</td>
<td>3085.2</td>
<td>3085.3</td>
</tr>
<tr>
<td>*012</td>
<td>2725.6</td>
<td>2725.5</td>
<td>2725.2</td>
</tr>
<tr>
<td>*111</td>
<td>2785.24</td>
<td>2785.3</td>
<td>…</td>
</tr>
<tr>
<td>400</td>
<td>…</td>
<td>…</td>
<td>4372.2</td>
</tr>
<tr>
<td>202</td>
<td>…</td>
<td>…</td>
<td>4142.7</td>
</tr>
<tr>
<td>*004</td>
<td>…</td>
<td>…</td>
<td>4000.4</td>
</tr>
<tr>
<td>301</td>
<td>…</td>
<td>4252.3</td>
<td>4252.3</td>
</tr>
<tr>
<td>*103</td>
<td>4026.0</td>
<td>4026.9</td>
<td>4026.9</td>
</tr>
<tr>
<td>310</td>
<td>…</td>
<td>…</td>
<td>3964.2</td>
</tr>
<tr>
<td>*112</td>
<td>…</td>
<td>…</td>
<td>3743.9</td>
</tr>
<tr>
<td>211</td>
<td>3849.4</td>
<td>3850.2</td>
<td>3850.7</td>
</tr>
<tr>
<td>*013</td>
<td>3697.1</td>
<td>3697.1</td>
<td>3696.7</td>
</tr>
<tr>
<td>220</td>
<td>…</td>
<td>…</td>
<td>3564.3</td>
</tr>
<tr>
<td>022</td>
<td>…</td>
<td>…</td>
<td>3390.6</td>
</tr>
<tr>
<td>121</td>
<td>3457.5</td>
<td>3458.1</td>
<td>3458.2</td>
</tr>
<tr>
<td>*104</td>
<td>…</td>
<td>…</td>
<td>4934.0</td>
</tr>
<tr>
<td>*005</td>
<td>…</td>
<td>…</td>
<td>4919.2</td>
</tr>
<tr>
<td>*014</td>
<td>…</td>
<td>…</td>
<td>4837.6</td>
</tr>
<tr>
<td>*113</td>
<td>…</td>
<td>…</td>
<td>4670.1</td>
</tr>
</tbody>
</table>

* Important for COCHISE

As already mentioned, the Table 1 listing is not complete, but restricted so as to concentrate on those levels relevant to the COCHISE experiment. The levels taken to be most significant for COCHISE are marked with an asterisk and consist of the following:

a. levels (0, 0, v₃), ≤ 5
b. levels (1, 0, v₃), ≤ 4
c. levels (0, 1, v₃), ≤ 4
d. levels (1, 1, v₃), ≤ 3
The rationale for choosing these levels is based on the assumption that the $v_1$ and $v_3$ modes are thermally equilibrated with each other (with a bath temperature of 80°K)\(^2\) in COCHISE prior to observation of the emission; this is because the rate of exchange of quanta between the $v_1$ and $v_3$ modes is expected to be on the order of gas kinetic. Since this process occurs without gain or loss of quanta, we conclude that all levels having the same value of ($v_1 + v_3$) are thermally equilibrated.

From the computed energy levels, it is readily shown that levels having $v_1 \geq 2$ are negligibly populated given this condition. The levels having $v_2 = 0$ which are appreciably populated are thus type a and b levels. Similarly, the levels having $v_2 = 1$ which are of significance are the type c and type d levels. If necessary, the calculation may be extended to include levels having $v_2 \geq 2$.

The transition frequencies in cm\(^{-1}\) for the aforementioned levels are given in Figure 1. The figure also shows schematically the kinetic coupling between the levels, previously discussed, namely,

$$(1, v_2, n) \longleftrightarrow (0, v_2, n+1).$$  \hspace{1cm} (1)

The population ratio of these levels is fixed by the bath temperature. In Figure 1, the expected ratio for a bath temperature of 80°K is indicated. The adjustable parameters required to fit the COCHISE spectrum can be reduced to a manageable number by using fixed ratios between certain level populations.

3. **EINSTEIN COEFFICIENTS FOR OZONE**

The problem of calculating accurate Einstein coefficients for an anharmonic, coupled triatomic molecule, such as ozone, is a formidable one. Both a suitable potential surface and dipole moment function are required as a starting point. The full quantum mechanical solution may then be obtained in principle, using the variational method. In practice, however, due to necessary limitations on the size of the basis set, only the lower vibrational levels may be treated accurately. A new semiclassical approach may be a promising alternative to the full quantum treatment.\(^8\) The accuracy of this approach appears to be limited primarily by the uncertainty in the dipole moment function.

We consider here some approximate qualitative models. The simplest model, which is nonetheless adequate for many situations, utilizes a harmonic oscillator (that is, assumes "mechanical harmonicity"). We also assume, for the moment, "electrical harmonicity," which means that only the first order dipole matrix element $|\langle \psi_f | q | \psi_i \rangle|^2$ is considered (q is a vibrational coordinate). The behavior of the Einstein coefficient for this case is given by

$$
\left( \frac{\nu_{001} \rightarrow 000}{\nu} \right)^3 \frac{A_{v_3 \rightarrow v_3-1}}{A_{001 \rightarrow 000}} = v_3
$$

(independent of $v_1$ and $v_2$); $A_{001 \rightarrow 000}$ is known accurately, $^2$ and $\nu$ appears in Table 1. This formula was used in Reference 2 for a preliminary analysis of the COCHISE data.
An appreciably more accurate result is given by evaluating the first order matrix element in the basic set of wave functions that were obtained when the perturbation matrix was diagonalized. This procedure takes into account much of the mechanical anharmonicity actually present. The results are given in Table 2 in the column "Perturbed Harmonic." For comparison, Eq. (4) is given in the "Unperturbed Harmonic" column. It is seen that the Darling-Dennison perturbation has a significant, although not drastic, effect on the Einstein coefficients.

### Table 2. (Matrix Element) × 2 for Δv₃ = -1 Transitions

<table>
<thead>
<tr>
<th>Eq. (4)</th>
<th>Unperturbed Harmonic</th>
<th>Perturbed Harmonic</th>
</tr>
</thead>
<tbody>
<tr>
<td>000 → 000</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>002 → 001</td>
<td>2</td>
<td>1.93</td>
</tr>
<tr>
<td>101 → 100</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>011 → 010</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>003 → 002</td>
<td>3</td>
<td>2.75</td>
</tr>
<tr>
<td>102 → 101</td>
<td>2</td>
<td>1.89</td>
</tr>
<tr>
<td>012 → 011</td>
<td>2</td>
<td>1.94</td>
</tr>
<tr>
<td>111 → 110</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>004 → 003</td>
<td>4</td>
<td>3.40</td>
</tr>
<tr>
<td>103 → 102</td>
<td>3</td>
<td>2.69</td>
</tr>
<tr>
<td>013 → 012</td>
<td>3</td>
<td>2.79</td>
</tr>
<tr>
<td>112 → 111</td>
<td>2</td>
<td>1.91</td>
</tr>
<tr>
<td>005 → 004</td>
<td>5</td>
<td>3.81</td>
</tr>
<tr>
<td>104 → 103</td>
<td>4</td>
<td>3.41</td>
</tr>
<tr>
<td>014 → 013</td>
<td>4</td>
<td>3.50</td>
</tr>
<tr>
<td>113 → 112</td>
<td>3</td>
<td>2.73</td>
</tr>
</tbody>
</table>

A somewhat unexpected phenomenon results from the Darling-Dennison perturbation which may be of some importance. A small but nonnegligible intensity in the (Δv₃ = -3, Δv₁ = 2) sequence, lying to the red of the main v₃ progression, is predicted. The quantity

\[
\left( \frac{v_{011} \rightarrow 000}{v} \right)^3 \frac{A(v_{1, v_2', v_3'}) \rightarrow (v_{1, v_2', v_3'-3})}{A_{001 \rightarrow 000}}
\]

(5)
is presented in Table 3 along with the transition frequencies. These values are compared with Table 2 intensities in Figure 2. The important thing to note is the borrowing of intensity by the new sequence from the "allowed" $\Delta v_3 = -1$ progression, especially at high $v$. This is a general, qualitative feature of mechanically anharmonic systems.

Table 3. $(\Delta v_3 = -3, \Delta v_2 = 2)$ Transitions

<table>
<thead>
<tr>
<th>Transition</th>
<th>(Matrix Element) $\times$ 2</th>
<th>$\nu$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>003 $\rightarrow$ 200</td>
<td>0.120</td>
<td>844.7</td>
</tr>
<tr>
<td>013 $\rightarrow$ 210</td>
<td>0.100</td>
<td>812.9</td>
</tr>
<tr>
<td>103 $\rightarrow$ 300</td>
<td>0.144</td>
<td>735.6</td>
</tr>
<tr>
<td>004 $\rightarrow$ 201</td>
<td>0.476</td>
<td>814.7</td>
</tr>
<tr>
<td>014 $\rightarrow$ 211</td>
<td>0.417</td>
<td>788.2</td>
</tr>
<tr>
<td>104 $\rightarrow$ 301</td>
<td>0.467</td>
<td>681.7</td>
</tr>
<tr>
<td>005 $\rightarrow$ 202</td>
<td>0.865</td>
<td>776.5</td>
</tr>
</tbody>
</table>

Figure 2. Relative Vibrational Intensities for Emitting Levels Using (a) Unperturbed Harmonic Oscillator and (b) Harmonic Oscillator Perturbed by Darling-Dennison Resonance
The important effect of electrical anharmonicity has not been included in the foregoing discussion. By analogy with diatomic molecules, it is expected that this will lead to a further decline in the value of the $\Delta v_3 = -1$ Einstein coefficient at high $v$. Consequently, the numerical values in Table 2 computed for the electrically harmonic case should be treated as a first approximation. In a qualitative sense, however, it does predict the general behavior of decreasing intensity with $v$ relative to the simple scaling given in Eq. (4).

4. ULTRAVIOLET INVESTIGATIONS OF OZONE

It may at first appear that the conditions of high pressure used in the UV studies preclude their direct application to the study of the recombination in the upper atmosphere. The actual case is quite the contrary, however. Since the high pressure experiments provide accurately measured concentrations of $O_2$, $O$ and $O_3$, fundamental rate coefficients for vibrational quenching may be extracted. Furthermore, the UV absorption spectra, unlike the IR emission spectra, show the population of the ground vibrational level as well as excited states. Finally, higher pressures can be actually more conducive, under some conditions to the observation of the nascent vibrational distribution. This is because in an initially pure oxygen experiment, ozone is formed in a three-body reaction whose rate is proportional to $[O_2]^2$ whereas the excited ozone is collisionally relaxed in a two-body interaction proportional to $[O_2]$.

We present here a preliminary analysis of the Hartley UV absorption spectrum based on a Franck-Condon synthesis. Both ab initio calculations and experimental data are used for verification of the results. Spectra of both ground and vibrationally excited levels are displayed, and a very simple application of the results to recombination data is also discussed. A full presentation of computational details will await further refinements.

Since only low $v$ levels of the ground state are considered here, the shapes of the upper ($^1B_2$) and lower ($^1A_1$) potential surfaces in only a small localized Franck-Condon region control the UV spectrum. Quadratic approximation to the local surfaces has therefore been used. The relative activities of the three normal modes, $q_1$, $q_2$, and $q_3$, can be estimated from ab initio calculations, absorption spectra, and resonance Raman spectra. The Raman data indicate that the bending mode, $q_2$, is essentially inactive. A similar conclusion was reached by considering the absorption spectrum. Accordingly, potential terms in $q_2$ may be removed, resulting in the following 2-dimensional, separable expressions for the local surfaces:

(Due to the length of References 9, 10 and 11, they will not be listed here. See References, page 21.)
\[ V^{1B_2} = \frac{k_1'}{2} (q_1 - \delta)^2 + \frac{k_3'}{2} q_3^2 \]  
\[ V^{1A_1} = \frac{k_1'}{2} q_1^2 + \frac{k_3'}{2} q_3^2 \]  

where \( q_1 \) and \( q_3 \) are symmetric and asymmetric stretch normal coordinates, respectively; \( k_1' \) and \( k_3' \) are the known force constants for the ground state; \( k_3' \) is known from the ab initio calculations\(^9\) and from the resonance Raman spectrum,\(^{11}\) \( k_3' \approx -3 k_3'' \). The main determinants of the shape of the ground state spectrum are \( k_1' \) and \( \delta \). They can be adjusted for a best fit. In this preliminary work, \( k_1' = 1.21 k_1'' \), and \( \delta = 2.507 \) in dimensionless units. Franck-Condon factors resulting from Eqs. (6) and (7) may be readily evaluated by a convolution of 1-dimensional overlap integrals. The latter were evaluated for the (harmonic) \( q_1 \) coordinate, and numerically for the \( q_3 \) coordinate via integration of the Schrödinger equation to obtain \( q_3 \) wavefunctions. The model embodied in Eqs. (6) and (7) has also been discussed previously in connection with dissociation of triatomic molecules.\(^{12,13}\) Although the surfaces given in Eqs. (6) and (7) using the parameter values specified are not ideal, the match between the observed and calculated ground state spectrum, \( \epsilon_{000} \) (Figure 3) is still very good. Absorption spectra of the \( 1\nu_1 \) and \( 1\nu_3 \) levels are presented in Figure 4. The spectrum of \( 1\nu_2 \) is assumed to be the same as the ground state spectrum.

It has been found experimentally that the \( 1\nu_1 \) and \( 1\nu_3 \) level populations equilibrate rapidly, reaching a population mixture determined by the bath translational temperature.\(^4,5,14\) The spectrum of this mixture \( \epsilon^* \), is therefore the experimentally relevant quantity characterizing the singly excited stretching modes. This point has been discussed more fully in connection with IR laser excitation experiments.\(^5\) In those experiments the determination of \( \epsilon^* \) was hampered by inadequate knowledge of the amount of vibrationally excited ozone produced by the IR laser. However, a quantity proportional to \( (\epsilon_{000} - \epsilon^*) \) was measured. Given a calculated \( \epsilon^* \) spectrum, an experimentally determined \( \epsilon^* \) spectrum can be matched to it by adjusting the constant of proportionality. In Figure 5, the laser data,\(^5\) adjusted as described, is compared to the current calculation of the room temperature \( \epsilon^* \). The agreement is very good, and within the experimental error of the measurements.

\[ \text{(6)} \]
\[ \text{(7)} \]

---


Analogous to the singly excited stretch spectrum, $\epsilon^*$, is the doubly excited stretch spectrum, $\epsilon^{**}$; $\epsilon^{**}$ is broader and redder than $\epsilon^*$, and essentially unstructured. It thus appears that $\epsilon_{000}^*$, $\epsilon^*$, and $\epsilon^{**}$ are sufficiently distinctive in shape that the corresponding vibrational populations can be extracted accurately from the Reference 4 spectra.

Bair and co-workers$^{4b, 4d}$ have demonstrated that the use of calculated UV spectra (similar to those in Figure 4) in modeling the observed ozone spectrum enables the extraction of vibrational level populations and relaxation rates during the recombination reaction. An improved analysis of Reference 4 data based on Franck-Condon calculations will be the subject of future work. Further refinements of the current Franck-Condon calculations are in progress; they are expected to yield more reliable spectra.

The type of information that a full UV analysis can yield may be demonstrated by the following simpler approach based on rough spectral shapes.$^{4a, 15}$ Given a

---

pair of potential surfaces, such as those specified by Eqs. (5) and (6), exact analytical expressions for the mean frequency $\bar{h}v$ and mean square frequency $(h\nu)^2$ as a function of vibrational energy may be derived. These quantities are defined by

$$\bar{h}v = \frac{\int I(\nu)/\nu \ h\nu \ d\nu}{\int I(\nu)/\nu \ d\nu} \quad (8)$$

$$\frac{1}{(h\nu)^2} = \frac{\int I(\nu)/\nu \ h\nu^2 \ d\nu}{\int I(\nu)/\nu \ d\nu} \quad (9)$$

where $I(\nu)$ is the absorption coefficient. The spectral variance $\sigma^2$ is given by
The spectral "width" is defined by the square root of the variance. The spectral position and shape may be characterized by the quantities $\hbar \nu$ and $\sigma^2$.

With use of Eqs. (6) and (7) for the potential surfaces, the following conclusions may be drawn:

1. The ozone UV absorption spectrum exhibits a red shift in proportion to the quantity of energy in the $\nu_3$ mode, $(E_3)$.
2. The spectrum exhibits an increase in variance proportional mainly to the quantity of energy in the $\nu_1$ mode $(E_1)$.
3. The spectrum is unaffected by the energy in the $\nu_2$ mode.

The behavior described in the foregoing is seen in the Figure 4 calculated spectra, and is also consistent with available experimental data. Given reliable potential surfaces, the absolute quantities of energy present in the $\nu_1$ and $\nu_3$ modes may be deduced from an ozone recombination spectrum.
The amount of energy in $\nu_3$ relative to $\nu_1$ in nascent ozone is an important question arising from the COCHISE study, and an issue that may be examined in the light of UV data. As explained previously, the relevant spectra are $\epsilon^*$, $\epsilon^{**}$, and so on, which are spectra of mixtures of levels having the same total number of stretching quanta. As collisional deactivation proceeds (following the initial ozone formation) the ratio $(E_3)/(E_1)$ should approach the value characteristic of the $\epsilon^*$ mixture. At earlier times, higher $\nu$ levels may be populated, in which case $\nu_3 \rightarrow \nu_1$ equilibration yields higher $(E_3)/(E_1)$ values due to the details of the energy level spacings. Therefore, at short times after the ozone is formed, the quantity (red shift)/(change in $\sigma^2$), which is proportional to $(E_3)/(E_1)$, may be considerably higher than at longer times.

In Figure 6 the data of Reference 4a has been treated by the preceding method. The large value of $(E_3)/(E_1)$ at short times indeed suggests that most of the vibrational excitation is initially distributed in $\nu_3$, consistent with the expected population of high $\nu$ levels. However, after $\sim 50\mu$sec the vibrational manifold is sufficiently relaxed so that most of the stretching mode excitation is in singly excited levels.

![Figure 6](image)

Figure 6. (Red Shift)/(Change in $\sigma^2$) vs Time After Photolysis of a 0.02 Torr O$_3$/115 Torr O$_2$ Mixture
The present preliminary study suggests that a detailed analysis of UV data on the ozone recombination will yield the following information:

1. An estimate for the absolute amount of energy $(E_1 + E_3)$ deposited in nascent ozone.

2. A rate constant for quenching of vibrational energy $(E_1 + E_3)$ by molecular oxygen.

3. The temporal dependence of the populations in levels $1\nu_1$, $1\nu_3$, $2\nu_1$, $2\nu_3$, $1\nu_1 + 1\nu_3$, and the ground state, for the experimental conditions of Reference 4. Appropriate scaling to lower pressures for atmospheric applications should be possible.


