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# Rotational structure in the near-infrared absorption spectrum of ozone

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Ozone absorption spectra near  $1\text{ }\mu\text{m}$  exhibit fine structure indicative of rotational subbands, suggesting that the upper electronic state is metastable. Preliminary analysis supports a previous assignment to the  ${}^3A_2 \leftarrow {}^1A_1$  transition. A binding energy of  $\sim 0.1\text{ eV}$  is inferred from the breakoff in the observed structure.

## I. INTRODUCTION

The factors controlling ozone's distribution in the atmosphere have been the subject of intensive study since the early 1970s. Since then our understanding of this molecule has improved greatly, yet there are many puzzling phenomena that suggest there is still room for improvement. A variety of spectroscopic, kinetic, and isotopic anomalies have been reported that appear to require the participation of certain unknown metastable electronic states in one way or another.<sup>1-5</sup>

The existence of such low-lying states has been predicted by *ab initio* electronic structure calculations for years,<sup>6-12</sup> but decisions about the stability of these states have been frustrated by the small binding energy of ozone ( $D_e = 1.13\text{ eV}$ ,  $D_o = 1.05\text{ eV}$ ) and the relatively large uncertainties typical of such calculations ( $0.1\text{--}0.2\text{ eV}$ ). Experimentally the situation has not been much better. Transitions to these states are spin and/or symmetry forbidden from the ground state and are therefore very weak. Moreover, except for the Huggins bands<sup>13</sup> the entirety of ozone's known electronic absorption spectrum, which extends from the Wulf bands near  $1\text{ }\mu\text{m}$  to beyond the Hartley bands in the UV, is apparently devoid of structure finer than diffuse vibronic undulations<sup>14,15</sup> presumably due to the prompt dissociation of the upper electronic states involved.

Here we report the first absorption spectra outside the Huggins bands that clearly show structure much finer than this,<sup>16</sup> and suggest that it is probably associated with molecular rotation in the lowest two vibrational levels available on the  ${}^3A_2$  electronic surface.

## II. EXPERIMENT AND RESULTS

Spectra were recorded with the dual-beam absorption instrument described previously with the addition of a multipass absorption cell to provide optical paths of  $\approx 23\text{ m}$  and the occasional use of a LN<sub>2</sub>-cooled germanium detector to enhance sensitivity at longer wavelengths.<sup>17,18</sup> Ozone pressures of 100–250 Torr provided adequate signal-to-noise levels for recording spectra at  $1.6\text{ nm}$  (ca.  $16\text{ cm}^{-1}$ ) resolution.

A typical spectrum is shown in Fig. 1. The inset shows published spectra for the Chappuis (ca.  $17\text{ }000\text{ cm}^{-1}$ ) and Wulf (ca.  $12\text{ }000\text{ cm}^{-1}$ ) band systems<sup>17,18</sup> to provide a

context for the present work, which is given in the main part of the figure. This spectrum focuses on the first few members of a long progression in the upper state bending mode, and the bands are labeled by their respective quantum numbers. The 1–1 band was identified by its location as well as its isotope shift and is reported here for the first time.

## III. DISCUSSION

The most striking feature of the spectrum is the presence of fine structure in each of the 1–1, 0–0, and 1–0 bands, and the absence of it in the 2–0. The character of this structure and its similarity across the three vibrational bands suggests that it is due to rotational transitions. This can occur only if the lifetime of the upper electronic state is long enough for the molecule to rotate a number of times prior to dissociation. Since previous measurements of the

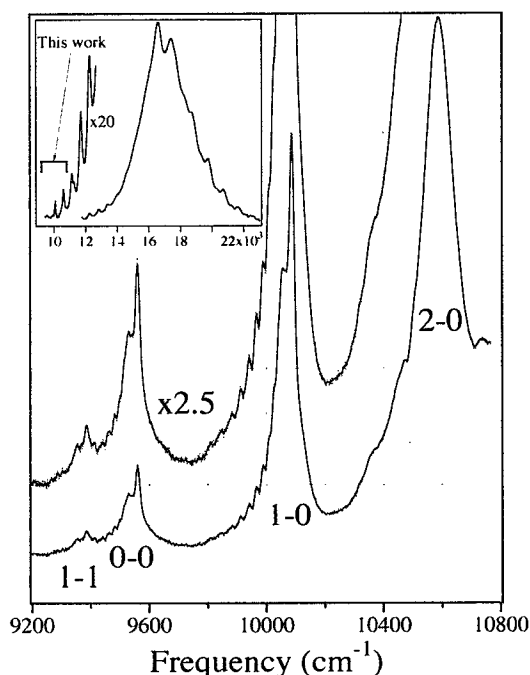


FIG. 1. Ozone absorption spectrum near  $1\text{ }\mu\text{m}$ . Inset shows the Chappuis and Wulf systems for perspective. Labels indicate vibrational assignments, and refer to bending mode excitation.

TABLE I. Molecular geometries (from Refs. 11 and 12) and rotational constants used in simulating rotational subband structure. The  $b$  and  $C_{20}$  axes coincide; the  $c$  axis is perpendicular to the molecular plane.

State	$r_e(\text{\AA})$	$\theta_e(^{\circ})$	$A(\text{cm}^{-1})$	$B$	$C$
$^1A_1$	1.277	116.1	3.496	0.441	0.392
$^3B_2$	1.360	108.3	2.470	0.430	0.366
$^3A_2$	1.348	101.5	2.155	0.480	0.392

adiabatic electronic energy place this state significantly above the  $\text{O} + \text{O}_2(v=0)$  asymptote we conclude that it is metastable. The barrier to dissociation apparently lies between the first and second vibrational levels, implying a binding energy somewhere between  $530$  and  $1060\text{ cm}^{-1}$ , or  $\sim 0.1\text{ eV}$ .

The preceding remarks are, of course, predicated on the assumption that a single electronic transition is responsible for both the unstructured as well as structured bands in the vibrational progression. Alternatively, it is possible that these systems are associated with two different upper electronic states, but the similarity of the vibronic isotope shifts of these bands<sup>17</sup> would require these two states to have very similar adiabatic energies. Further evidence for the single-state hypothesis is presented below.

Braunstein and Pack recently performed calculations of ozone's absorption spectrum in this region based on *ab initio* potential energy surfaces for the  $^1A_1$ ,  $^1A_2$ , and  $^3A_2$  states.<sup>12</sup> Transitions to the  $^1A_2$  state produced a weak, featureless continuum, while absorption to the  $^3A_2$  lead to pronounced vibrational structure associated with excitation of bound  $\nu_1$  and  $\nu_2$  motions on the upper surface. The predicted vibrational bands and their assignments resemble the experimental spectrum quite closely, although the assumption that  $\nu_3$  motion is purely dissociative makes the calculated spectrum smoother than the spectrum we observe even where the fine structure reported here is absent. The singlet-triplet transitions apparently become allowed through a spin-orbit interaction,<sup>12</sup> with the  $^3A_2 \rightarrow ^1A_1$  transition probability about two orders of magnitude larger than that for the  $^3B_2 \rightarrow ^1A_1$ .<sup>19</sup>

To investigate the validity of our assignment of the fine structure to rotational transitions we have performed a simple simulation using rotational constants derived from the *ab initio* geometries given in Refs. 11 and 12; the relevant data are presented in Table I. The molecule is a near-prolate top in any of the three states listed ( $b \approx 0.01$ ,  $\kappa \approx 0.95$ ), but due to the large geometry changes associated with the electronic transitions and the relatively low resolution employed, it is sufficient to treat the molecule as a prolate top ( $C = B$ ) for which the rotational transition frequencies are given by Eq. (1):<sup>20</sup>

$$\nu_{\text{rot}} = B'J'(J'+1) - B''J''(J''+1) + (A' - B')K'^2 - (A'' - B'')K''^2. \quad (1)$$

The single and double primes refer to the upper and lower states, respectively, and centrifugal distortion effects have not been included. Here,  $A \gg B$  and the corresponding spectrum consists of a series of subbands whose origins are

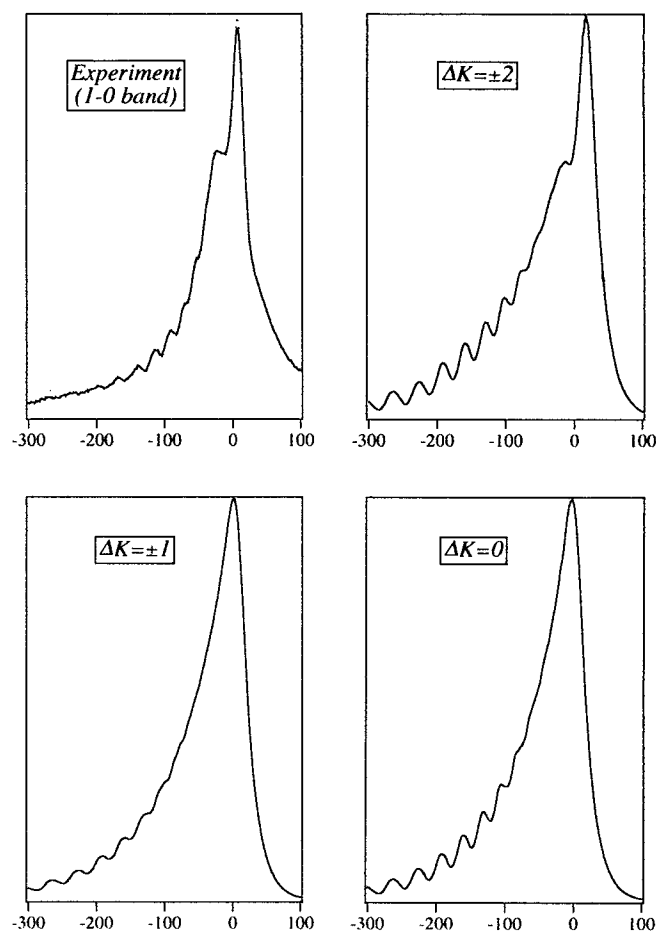


FIG. 2. Comparison of experimental observations for the 1-0 band with simulated rotational subband structure for  $\Delta K=0, \pm 1$ , and  $\pm 2$  selection rules. The frequency scale for the experimental spectrum is that of Fig. 1 less  $10\,080\text{ cm}^{-1}$ .

described by the last two terms; the first two terms and the small splittings neglected in our symmetric rotor treatment determine the internal structure of the subbands, which goes nearly unnoticed at our resolution. From the values of  $B$  given in the table for the  $^1A_1$  and  $^3A_2$  states one can see that the individual subbands will be shaded to the blue. We have therefore simply convolved a  $q$ -branch line spectrum with our instrumental bandpass to approximate their internal structure, and except for this approximate shape factor we have treated the subbands as "lines." Intensities were calculated taking account of the lower state population and degeneracy, and the selection rules appropriate for a singlet-triplet transition,  $\Delta K=0, \pm 1, \pm 2$ ,<sup>20</sup> were investigated separately. The resulting spectra are shown in Fig. 2 together with the experimental observations for the 1-0 band.

While we have clearly not achieved quantitative agreement (nor would we expect to at this level of "theory"), the qualitative similarities between the calculated and experimental spectra are striking and at least two features are worthy of discussion. First, the bimodal character of the band peak, clearly apparent in the experimental spectrum, arises only in the calculated spectrum for the  $\Delta K = \pm 2$

selection rule through its control of the separation between the lowest  $K$  subbands. This selection rule is only available for singlet-triplet transitions. The  $\Delta K=0, \pm 1$  selection rules result in what appears to be a single peak in the calculated spectra, but it is conceivable that coincidences between low- $K$  sub-bands for slightly different molecular geometries may also account for this bimodal shape.

Second, the positions of the subbands given by Eq. (1) for the  $\Delta K = \pm n$  selection rules are

$$\begin{aligned} \nu_{\text{rot}}(\Delta K = +n) &= ((A' - B') - (A'' - B''))K''^2 \\ &+ (A' - B')(1 + 2nK''), \quad K'' \geq 0 \end{aligned}$$

and

$$\begin{aligned} \nu_{\text{rot}}(\Delta K = -n) &= ((A' - B') - (A'' - B''))K''^2 \\ &+ (A' - B')(1 - 2nK''), \quad K'' \geq n \end{aligned} \quad (2)$$

for  $n=0, 1$  or  $2$ . The quadratic coefficient of a parabolic fit to plots of band position vs  $K''$  (or even  $K''+x$  where  $x$  is a constant) yields information on the quantity  $(A' - B') - (A'' - B'')$ . From the data in Table I this coefficient should be  $1.38 \text{ cm}^{-1}$  for a transition to the  $^3A_2$  state, and  $1.02 \text{ cm}^{-1}$  for the  $^3B_2$ . The six subbands discernable in the red wing of the 1-0 transition yield a coefficient of  $1.4 \pm 0.1 \text{ cm}^{-1}$ , consistent with the association of these features with the  $^3A_2$  rather than the  $^3B_2$  state. This conclusion must be regarded with some caution since the underlying structure is sure to be more complex than such a simple analysis assumes, and our neglect of centrifugal distortion effects may not be justified if the state is so weakly bound. Higher resolution spectra are obviously needed for a complete understanding of these subbands.

#### IV. CONCLUSIONS

The lowest energy members of the near-IR absorption bands of ozone possess fine structure which is probably due to rotation of the molecule in the upper vibronic state, suggesting that this state is metastable. To our knowledge this is the first spectroscopic evidence which has been reported for the existence of such a state. A preliminary analysis of the structures as rotational subbands lends support to a recent theoretical assignment of the near-IR vibronic features to the  $^3A_2 \leftarrow ^1A_1$  electronic transition.

A number of areas should be explored in future work. First, we clearly need absorption data at higher resolution. There is little doubt that the underlying spectrum is complex, even if our rotational subband hypothesis is correct. A systematic exploration of the spectrum at successively higher resolutions would be invaluable for developing a complete understanding of it. We are currently working on obtaining the necessary spectra. Second, it would be interesting to know more about the possible role of this state in

atmospheric chemistry. Study of the absorption spectrum of the  $^3A_2$  state itself, perhaps in two-color transient absorption experiments, would help assess its role in photochemical processes as well as provide fundamental information on the higher-lying triplet states of ozone. A better measure of the state's binding energy, for example, would determine how accessible it is from thermal  $\text{O} + \text{O}_2$ , and measurement of a barrier height to dissociation presents a challenging opportunity for comparison with *ab initio* calculations of potential energy surfaces. Finally, active experiments which exploit optical population of this state could provide information on its possible role in producing some of the anomalous kinetic and isotopic behavior mentioned earlier. It is hoped that the present results will stimulate these areas of investigation.

#### ACKNOWLEDGMENT

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