

Near infrared absorption spectra of ozone by high resolution Fourier transform spectrometry

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Among the five lowest lying excited electronic states of ozone, the triplet 3A_2 has been identified and characterised by high resolution Fourier transform absorption spectrometry in the 10000 cm^{-1} region. This state is responsible of the Wulf transition and has two bound vibrational levels. The analysis of the rotational structure of one band of the $^3A_2 \leftarrow \tilde{X}^1A_1$ transition allows to determine: spectroscopic constants, geometry and lifetime of ozone in the (0,0,0) level of the 3A_2 state, absorption cross-sections in the 9500 – 11500 cm^{-1} range. Preliminary results are also given concerning the close 3B_2 state.

decades [1,2] to study structure, spectroscopy and excited states, all more or less related to the photochemistry of this molecule.

We are particularly interested in the lowest lying excited electronic states that determine absorption in the Near Infra-Red up to visible region. Some of them (metastable) could be sufficiently long-lived to constitute a potentially important atmospheric reservoir of “hidden” energetic ozone that may play a significant role in ozone recombination kinetics. They also could be responsible for a number of anomalies in O – O₂ photochemistry including kinetics as well as isotopic enrichment [3].

So contrarily to the UV region (Huggins and Hartley bands) for which absorption from the ground state is easily detected in the atmosphere (σ_a about 10^{-21} – 10^{-20} $\text{cm}^2/\text{molecule}$) and is of major importance for the study and monitoring of the atmospheric ozone layer, in the Near Infra-Red the absorption cross-sections are very weak (σ_a about 10^{-23} $\text{cm}^2/\text{molecule}$) according to the metastable character of

Absorption of radiation of ozone initiates important chemical transformation in the troposphere, stratosphere and mesosphere although a “minor” constituent. So extensive efforts were undertaken these last

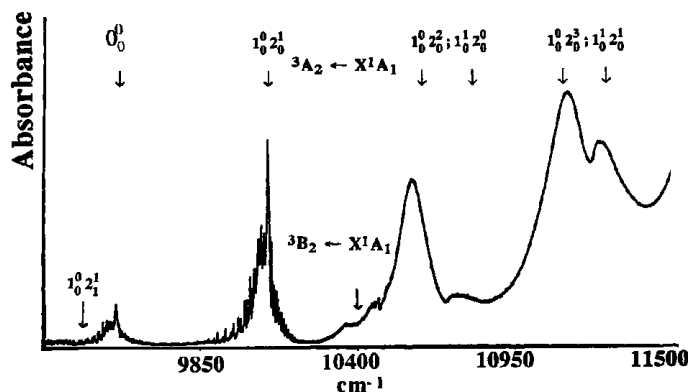


Figure 1. Absorption spectrum of ozone in the Near Infra-Red region and identification of different electronic transitions and vibrational bands at $T = 20\text{ }^\circ\text{C}$.

the states involved. So, the experimental technique requires particular conditions.

Experiments are so performed with a multipass “White” cell of one meter long (path to 160 metres), equipped with high reflectivity broadband mirrors which could be cooled to $-50\text{ }^\circ\text{C}$. Ozone (pressure 20 – 150 Torr) is produced by a 10 kV – 400 Hz electric discharge in a high purity oxygen gas ($^{16}\text{O}_2$ and $^{18}\text{O}_2$). The source is a stable halogen lamp and detector either a silicon avalanche or InGaAs photodiode dependant on the spectral region studied. High Resolution spectra were recorded in the 8600 – 11000 cm^{-1} range with a Bomem DA3 Fourier Transform spectrometer (resolution between 0.020 – 0.50 cm^{-1}) with recording time to 30 – 40 hours (Fig. 1).

- The 3A_2 state has two bound vibrational levels, bound by about 1000 cm^{-1} , the $(v'_1 = 0, v'_2 = 0, v'_3 = 0)$ level and the $(v'_1 = 0, v'_2 = 1, v'_3 = 0)$ level, the subscript $i = 1, 2$

or 3 designating the three respective vibrational modes of the ozone molecule (symmetric stretch bending and anti-symmetric stretch) [4a and 4b].

- Despite extremely congested spectra, we succeeded to obtain a rotational analysis of the 0_0^0 band ($(0,0,0) \leftarrow (0,0,0)$ transition) of $^{16}\text{O}_3$ (Fig. 2) and a polynomial development of the rovibrational energies of the $(0,0,0)$ level of the 3A_2 state [4b], the rovibrational energies of the \tilde{X}^1A_1 ground state of ozone being known with high precision [5]. So we determined the origin of the transition $T_0 = 9553.021(78)\text{ cm}^{-1}$, the bending frequency $\omega_2 = 530.78(18)\text{ cm}^{-1}$. The geometry relative to the 3A_2 state can be deduced from the rotational constants: bond length $r = 1345\text{ \AA}$ and bond angle $\theta = 98.9^\circ$, in good agreement with recent *ab initio* results [6,7].
- From experimentally measured absorption cross-sections of the least broadened lines, we determined relative Einstein coefficients from which we extracted the related lifetimes, using estimated Franck Condon factors [8]. If predissociation is neglected the lifetime is $0.2 \pm 0.1\text{ s}$, specific of a metastable state and close to *ab initio* values [9-10]; but rovibrational levels of the upper 3A_2 state seem more or less predissociated and if we take this effect into account, we found that the effective lifetime is drastically reduced to 10^{-9} s .
- The table I gives instead of σ_a the integrated absorption cross-sections σ'_a in $\text{cm}^2\text{ cm}^{-1}\text{ molecule}^{-1}$, (often used in the litterature) for the different vibrational bands observed near 10000 cm^{-1} .
- Concerning the 3B_2 state, it was recently identified [2,11] as responsible of the absorption band located in the 10300 – 10550 cm^{-1} range. Isotopic study done in the two previous references, for $^{16}\text{O}_3$ and $^{18}\text{O}_3$, allows to ascertain that the observed band of the $^3B_2 \leftarrow \tilde{X}^1A_1$ transition is a 0_0^0 band. The comparison of the simulation of a $^3B_2 \leftarrow ^1A_1$ transition and of the experimental spectrum (Fig. 3) allows to give a preliminary assignment for the

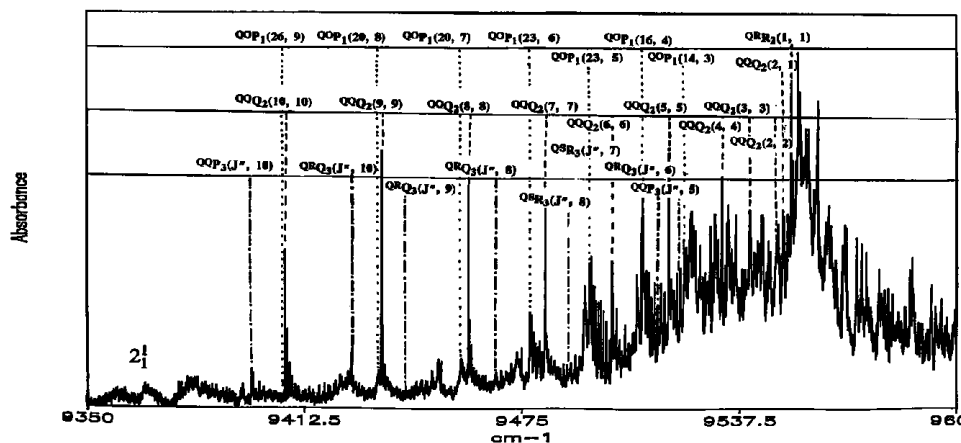


Figure 2. Overview of the assignments for the 0_0^0 band of the $^3A_2 \leftarrow \tilde{X}^1A_1$ transition of ozone. The triplet state is considered with a case (b) coupling and the standard spectroscopic notation is used for labeling branches and lines in triplet-singlet rotationally resolved spectra, i.e. $^{\Delta K \Delta N \Delta J} J'_E(J'', K'')$. The $^3A_2 \leftarrow \tilde{X}^1A_1$ transition of ozone follows the selection rules, $\Delta J = 0, \pm 1, \Delta N = 0, \pm 1, \pm 2, \Delta K_a = (\Delta K) = 0, \Delta K_c = 0, \pm 2$ ($K_c = J - K_a$ or $J - K_a + 1$). So for a $00P_1(26, 9)$ line, $\Delta K = 0, \Delta N = -2, \Delta J = -1$, the spin component of the triplet is $F_1(J = N + 1)$, $J'' = 26, K''_a = K'' = 9$. The experimental conditions were: $P = 20.5\text{ Torr}$, $T = -51\text{ }^\circ\text{C}$, absorption path length = 156 m, theoretical resolution 0.020 cm^{-1} , recording time = 35 hours.

Table I.

$\sigma'_a \times 10^{21}$	$0_0^0 + 2_1^0$	2_1^0	2_2^0	2_3^0	$1_1^0 0_0^0$	$1_0^0 0_0^0$	${}^3B_2^0(0_0^0)$
$T = -50\text{ }^\circ\text{C}$	0.7 ± 0.2	3.0 ± 0.4	6.5 ± 0.8	9.0 ± 5.0	1.8 ± 0.8	7.1 ± 2.0	0.9 ± 0.5
$T = +20\text{ }^\circ\text{C}$	0.8 ± 0.2	2.9 ± 0.4	5.9 ± 0.8	8.0 ± 5.0	2.0 ± 0.8	7.7 ± 2.0	0.8 ± 0.5

main absorption peaks, to determine the origin of the transition $T_0 = 10460\text{ (5) cm}^{-1}$ and the geometry of the 3B_2 state, bond length $r = 1.36\text{ \AA}$ and bond angle $\theta = 108^\circ$ very close to the ab initio results [6,7]. The ${}^3B_2 \leftarrow \tilde{X}^1A_1$ transition moment was more over predicted to be about 100 times smaller than the ${}^3A_2 \leftarrow \tilde{X}^1A_1$ transition moment [9] and the question of this small theoretical value remains opened.

In conclusion, high resolution spectrometry allowed to demonstrate that the 3A_2 state is responsible of the Wulf transition, it is a metastable state but its lifetime is considerably reduced by predissociation effect. With no doubt, collisions in the atmosphere will give rotational transfers to highly dissociative 3A_2 levels and the often postulated metastable state of ozone lying well below the dissociation limit of the

ground state does not seem to exist as a reservoir of “hidden” ozone. The 3B_2 state is also a predissociated state but in this case the line widths are so large than the rotational analysis of a so diffuse spectra is really difficult and the experimental conditions have to be sharply improved. Then, numerous points remain still to elucidate about the spectroscopy of these triplet states, their interactions with other electronic states and their dissociative nature. But, given the complexity of their structure and superpositions, it seems likely that investigations at low temperature (seeded supersonic jet) and in some cases (3A_2 state for example) technique such as intracavity laser spectroscopy [12] or cavity ring down spectroscopy [13] will clarify these points and provide new keys to the dynamics of their formation and dissociation.

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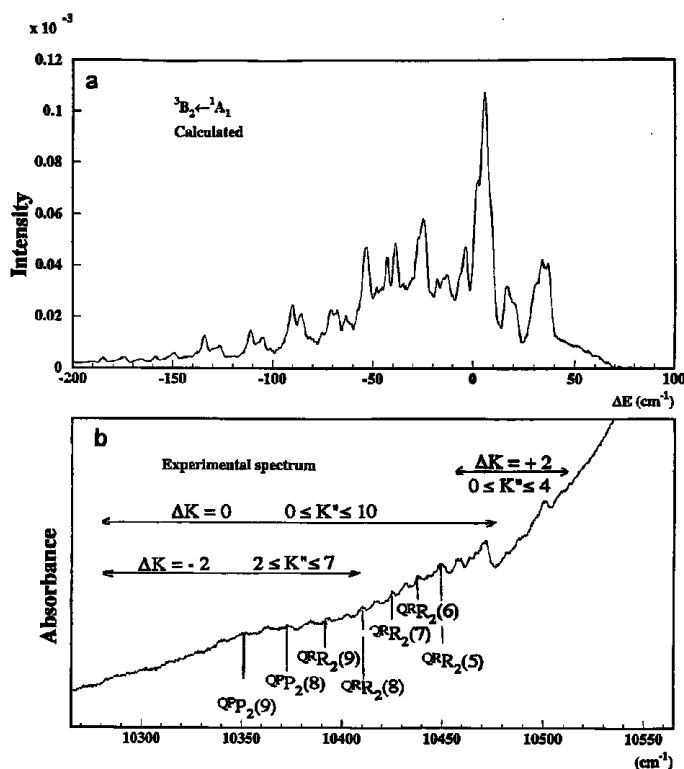


Figure 3. Comparison of the calculated spectra corresponding to a ${}^3B_2 \leftarrow X^1A_1$ transition with $r = 1.36\text{ \AA}$ $\theta = 108^\circ$; the full width at half maximum for the theoretical lines is 2 cm^{-1} . b) Absorption spectrum in the experimental conditions of figure 1. The selections rules on K_a and K_c for this transition type are $\Delta K_a = 0, \pm 2$ and $\Delta K_c = \pm 1, \pm 3$. Our rough model allows to obtain good coincidences between the main peaks of the calculated and experimental spectra and to give previous assignments for some of them.