Observation of the Zeeman Effect of Ozone by Doppler Free Laser Spectroscopy

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

The Zeeman effect of rotational-vibrational transitions of ozone has been studied with a CO₂ laser at 9.6 μm by means of saturation spectroscopy. The observed Zeeman pattern of the ν₃ transitions 16₈₉₉ – 16₈₉₈ and 11₃₂ – 12₃₃ are analyzed and compared with calculations. The previously proposed assignments are confirmed.

Introduction

During the past decade laser magnetic resonance has become a powerful tool in molecular spectroscopy of free radicals and molecular ions. Because of its high sensitivity it is an excellent method to investigate free radicals in very low concentrations and to measure their molecular constants with high precision. So far most of the radicals observed by radioastronomy have been investigated by LMR methods. We have begun the construction of a LMR spectrometer in order to analyze the spectra of radicals and ions of astrophysical interest by means of CO₂, N₂O and CO lasers.

For a variety of reasons, ozone was chosen as first target for investigation with the newly built LMR spectrometer.

(i) There exist several coincidences between strong O₃ absorption lines and several CO₂ laser lines [1, 2, 3].

(ii) The small (rotational) magnetic moment of O₃ allows a scrutinizing test of the spectrometer’s resolution. It also demonstrates the feasibility of LMR techniques even on closed shell molecules, which are mostly not taken into consideration for LMR experiments, and

(iii) In comparison with ions and radicals the handling of O₃ is easy. Since the molecular constants [4] and the magnetic moments along the principal axes [5] are known to high accuracy, the molecular Zeeman effect of the observed transitions can be calculated using the expressions given by Hüttner and Flygare [6] for asymmetric top molecules.

Experimental

Ozone was prepared using a silent electric discharge ozonizer. The resulting ozone-oxygen mixture was trapped at liquid nitrogen temperature and finally purified by pumping for several hours at this temperature. The total pressure in the gas cell did not increase due to formation of oxygen during periods of more than two hours.

The 15 cm cell was made of pyrex and BaF₂ windows were epoxied on both ends. The CO₂ laser has a conventional flowing discharge tube 120 cm in length and operates at pressures up to 30 Torr. Single frequency operation is obtained with a grating and a diaphragm inside the cavity selects a pure TEM₂₀ mode. The frequency can be tuned over 80 MHz on most of the lines by applying a dc voltage to the piezoelectric transducer carrying the output coupling mirror. The tuning corresponds to one free spectral range of the resonator.

A block diagram of the experimental arrangement is shown in Figure 1. The magnet (Bruker B-E 30 V) operates at fields up to 25 kG. The field is stabilized with a Hall probe and it can be determined accurately by means of a NMR gaussmeter. The cell is placed between the poles of the magnet and the variation of the field along the cell is less than 10 G at 20 kG.

Instead of using an intracavity setup mostly used in LMR studies, we have employed saturated absorption spectroscopy to observe the Zeeman splitting of the molecular transitions, because the small magnetic moment of O₃ prevents the use of the widely applied Zeeman modulation. Although the intracavity arrangement provides considerably higher sensitivity, the saturation method has advantages (i) Doppler-free-spectroscopy and (ii) the relative ease...
Observations

Absorptions of ozone have been reported with P(30) [3] and P(40) [2] of the 9.6 μm CO₂ laser band. A typical saturation signal at P(30) is shown in Fig. 2 at several field settings. The width of the signal is mainly determined by pressure broadening, although a small contribution of power-broadening cannot be excluded. In addition there is also some Doppler shaped broad feature present, which is probably due to heating by the absorbed laser power. For ozone this seems to be an unusually efficient process when compared with other molecules.

Only two components at high fields are observed indicating that the molecular $g$-values in both the vibrational excited state and the ground state are nearly the same. In [3] and [11] an assignment of this absorption is given with (001) $16_{8,9} - (000) 16_{8,8}$. Using the molecular constants of Barbe et al. [4] and the components $g_{aa}$, $g_{hh}$ and $g_{cc}$ of the $g$-factor given by Mack et al. [5] we calculate the $g_J$ factors of both levels to be $g_J = -0.8209$ yielding a splitting between $\sigma_+$ and $\sigma_-$ transitions of 25.7 MHz at 20530 G. This is in good agreement with our observed splitting. In addition no other nearby absorption in the table of Barbe et al. leads to a similar agreement, thus the assignment is unequivocally confirmed. The calculation did not include the higher order terms of the interaction with the magnetic field. A possible change of the magnetic moment in the vibrationally excited state is believed to be very small [10].

On P(40) the Zeeman pattern is less revealing. According to Young et al. [2] this ozone absorption is probably due to the transition (001) $11_{9,2} -$
(000) 129,3, which is supported by the newer data of Barbe et al. For the upper level we calculate $g_J = -1.8936$ and for lower $g_J = -1.6259$. Due to the different $g_J$ factors the Zeeman structure consists of 46 closely spaced transitions, which we have not been able to resolve. Accordingly at high fields we observe only one broad feature with an approximate halfwidth of 40 MHz, which is consistent with the calculated structure.

Further absorptions of O₃ and other CO₂ laser lines have not been observed, but it should be pointed out, that the assignments of several other lines found with a CO₂ waveguide laser [1, 3] could also be verified, if necessary, by observation of the Zeeman effect. This work will be extended to the investigation of free radicals and molecular ions.

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