

Vibronic spectrum of $^{15}\text{N}^{16}\text{O}_2$ between 415 and 440 nm

E.A. Volkers^a, J. Bulthuis^a, S. Stolte^a, R. Jost^b, N. Wehres^c, H. Linnartz^{c,*}

^a Department of Physical Chemistry, Laser Centre Vrije Universiteit, De Boelelaan 1083, NL 1081 HV Amsterdam, The Netherlands

^b Laboratoire de Spectrométrie Physique, Université Joseph Fourier de Grenoble, B.P. 87, F 38402 Saint Martin d'Hères Cedex, France

^c Sackler Laboratory for Astrophysics, Leiden Observatory, Postbus 9513, NL 2300 RA Leiden, The Netherlands

Received 12 March 2007; in revised form 30 May 2007

Available online 21 July 2007

Abstract

The time gated laser induced fluorescence (LIF) excitation spectrum of adiabatically cooled $^{15}\text{N}^{16}\text{O}_2$ has been measured close to the dissociation limit (22 700–24 050 cm^{-1}). The spectrum consists of numerous rotationally resolved vibronic bands with mainly irregular structures and consequently only an angular momentum labeling has been possible. These rotationally assigned isolated transitions, however, are highly suited for laser induced dispersed fluorescence spectroscopy (LIDFS) that gives spectroscopic access to the more regular parts of the electronic $^{15}\text{N}^{16}\text{O}_2$ spectrum. Accurate lists with transition frequencies—mainly R(0) and R(2) transitions—are provided. © 2007 Elsevier Inc. All rights reserved.

Keywords: Laser spectroscopy; Supersonic jet; Nitrogen dioxide; Vibronic spectra; Isotopic effects

1. Introduction

In the last three decennia the NO_2 molecule has been topic of intense spectroscopic research. The reason for this interest is twofold. On one side NO_2 is an atmospherically relevant species known to play a key role in a number of reaction schemes, both as a buffer gas (ozone depletion), as a precursor (e.g. NO formation upon photo-dissociation) and as a reactive intermediate (e.g. in the formation of HONO or HNO_3 that are precursors of acid rain) [1]. On the other side the interpretation of the visible and near-infrared spectrum has turned out to be a spectroscopic challenge. NO_2 seems to be a rather simple molecule—three atoms and a nearly symmetric top (coat-hanger like) molecular geometry—but the electronic NO_2 spectrum is highly complex. This is due to a vibronic coupling between the X^2A_1 electronic ground state and the first electronically excited A^2B_2 state via the anti-symmetric stretch coordinate with b_2 symmetry, favored by a rather low lying conical intersection ($\sim 10\,000\text{ cm}^{-1}$) between the potential energy surfaces of these two states. In fact, NO_2 has become a prototype mol-

ecule for studies of strong intramolecular couplings and statistical approaches have been used to handle the (vibronic) level spacing distribution that have characteristics of a chaotic systems [2,3]. A number of theoretical [4–9] and experimental [10–16] studies have addressed this problem. Laser induced dispersed fluorescence spectroscopy (LIDFS) [13], laser induced fluorescence (LIF) [14], cavity ring down [15] and bolometer [16] studies have provided a wealth of spectroscopic data. For the main isotopologue $^{14}\text{N}^{16}\text{O}_2$ this has resulted recently in a simulation of the time domain non-adiabatic dynamics of the molecule on the coupled X^2A_1 and A^2B_2 electronic states [17]. So far about 300 vibronic levels below and just above the conical intersection have been vibronically assigned [13], for higher energies identifications are still ambiguous and above $16\,500\text{ cm}^{-1}$ spectra are essentially vibronically chaotic [2,3].

The majority of the electronic studies of NO_2 have focused on the main isotopic species: $^{14}\text{N}^{16}\text{O}_2$. Large gas consumption has prohibited systematic studies of the less abundant isotopologues. In an experimental article we have reported the construction of an ultra-sensitive time gated LIF setup with a gas consumption as low as $0.5\text{ }\mu\text{mol}/\text{cm}^{-1}$ spectral range [18]. This has made possible the detection of hundreds of new bands in the

* Corresponding author. Fax: +31 71 5275819.

E-mail address: linnartz@strw.leidenuniv.nl (H. Linnartz).

12000–18000 cm^{-1} region of different $^x\text{O}^y\text{N}^z\text{O}$ isotopologues, such as $^{15}\text{N}^{16}\text{O}_2$, $^{16}\text{O}^{14}\text{N}^{18}\text{O}$ and $^{14}\text{N}^{18}\text{O}_2$ [19,20]. An extension to lower energies, i.e. to the more regular part of the potential well, has not been possible, particularly because of experimental limitations, such as weak transitions and low fluorescence yields in the near infrared. The present study, however, offers a way to overcome this problem by providing LIF data of high energetic transitions of $^{15}\text{N}^{16}\text{O}_2$ as a starting point for future LIDFS work. The LIF results provide accurate excitation frequencies below the dissociation limit [21] that are needed to record high resolution dispersed fluorescence spectra similar to the work on $^{14}\text{N}^{16}\text{O}_2$ [13]. LIDFS allows access deep into the potential well and is a powerful tool even though LIDFS spectra consist of only a few rotational lines when a supersonic jet is used. The results will be complementary to direct absorption studies that probe the vibrational ground state and the lowest vibrational levels and that are available for $^{15}\text{N}^{16}\text{O}_2$ from a number of mainly Fourier transform based microwave and infrared studies [22–26].

In this letter we provide accurate excitation frequencies for the $^{15}\text{N}^{16}\text{O}_2$ isotopologue at wavelengths between 415 and 440 nm. So far more than 250 rotationally resolved vibrational bands of the $\text{A}^2\text{B}_2\text{--X}^2\text{A}_1$ electronic transition have been observed for this isotopologue in the 14300–18000 cm^{-1} region applying LIF. A full rotational analysis has been possible for the majority of these bands [19]. The present work extends $^{15}\text{N}^{16}\text{O}_2$ spectroscopy into the 22700–24050 cm^{-1} region. It should be noted that the spectroscopy at these high energies is of a different nature, as the electronic spectra are essentially rovibronically chaotic. Nevertheless, the resulting experi-

mental frequencies and the corresponding rotational assignments are a prerequisite for laser induced dispersed fluorescence experiments that are needed to access the more regular (i.e. near infrared) part of the $\text{A}^2\text{B}_2\text{--X}^2\text{A}_1$ electronic spectrum.

2. Experiment

The experimental setup has been described in detail [18]. The third harmonic of a Nd:YAG laser is used to pump a tunable dye laser covering the appropriate frequency regime using Stilbene 3 dye with a typical bandwidth of about 0.1 cm^{-1} . The laser beam is focused onto an expanding beam of a mixture of 5% $^{15}\text{N}^{16}\text{O}_2$ and Ar. The $^{15}\text{N}^{16}\text{O}_2$ is produced in a standard synthetic procedure starting from 99% pure $\text{Na}^{15}\text{NO}_3$ [19,27]. The resulting isotopic purity is better than 95%. A small gas consumption is achieved by using a high intensity piezo electric pulsed molecular beam source that is optimized for a well-defined short pulse shape with an opening time of 150 μs . A photomultiplier tube, sensitive for 310–860 nm, is used to monitor the fluorescence zone that is about 1.5 cm downstream from the nozzle orifice. Cut-off filters are used to shield the detector from residual laser light. Typically 10 laser shots are averaged for each data point. The bandwidth of the pulsed laser system is the limiting factor in determining the absolute frequency accuracy for which a wavemeter is used. A conservative estimate yields an absolute frequency accuracy of 0.05 cm^{-1} . As the setup has been designed for fully automatic scanning over large frequency ranges an etalon signal with a free spectral range of 1.22 cm^{-1} is recorded to correct for non-linearities.

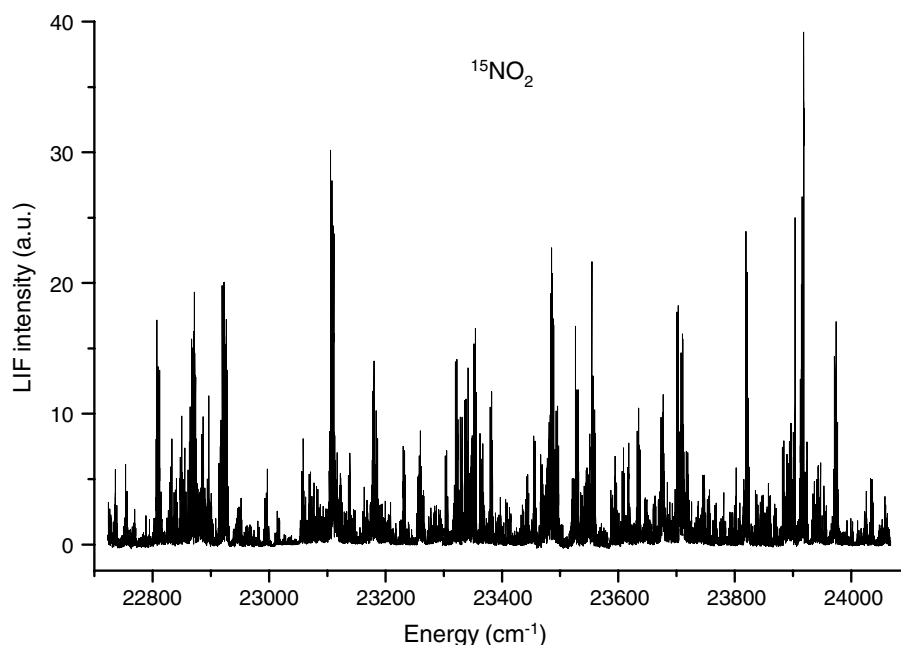


Fig. 1. An overview scan of the electronic spectrum of $^{15}\text{N}^{16}\text{O}_2$ in the 415–440 nm region recorded by time gated LIF spectroscopy. The intensities are normalized on the absorption cross section (assuming constant fluorescence detection efficiency). The general features (spectral density and intensity distribution) are similar to those previously observed for the main isotopologue.

Download English Version:

<https://daneshyari.com/en/article/5415844>

Download Persian Version:

<https://daneshyari.com/article/5415844>

[Daneshyari.com](https://daneshyari.com)