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N₂O weak lines observed between 3900 and 4050 cm⁻¹ from long path absorption spectra

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Abstract

Previously unobserved nitrous oxide transitions around 2.5 μm are measured by intracavity laser absorption spectroscopy (ICLAS) analyzed by time-resolved Fourier transform (TRFT) spectrometer. With an accuracy of the order of 10^{-3} cm^{-1} , measured positions of 1637 assigned weak transitions are provided. They belong to 42 vibrational transitions, among which 33 are observed for the first time. These data are believed to be useful in particular to monitoring atmosphere purposes.

In this note, intracavity laser absorption spectroscopy (ICLAS) coupled (1) with time-resolved Fourier transform (TRFT) spectrometer is applied to the measurement of previously unobserved N₂O transitions around 2.5 μm . High resolution absorption spectra of N₂O in natural isotopic abundance are recorded around 4000 cm^{-1} with kilometric absorption path lengths. Their analysis reveals the observed weak transitions belong to 42 vibrational transitions, among which 33 are observed for the first time. These data are believed to be useful in particular for atmospheric applications.

The laser, installed in a vacuum chamber, is made of Cr²⁺: ZnSe amplifying medium inserted in X-fold cavity. It is optically pumped with an Er³⁺ fiber doped laser emitting at 1.6 μm . The pumping beam is chopped by an acousto-optic modulator. The laser build-up is recorded with a TRFTS equipped with two InSb detectors cooled at 77 K. More details on the experimental setup may be found in the instrumentally oriented paper (2) and in (3) where new data measurements and analysis for 23 C₂H₂ molecular bands located around 4000 cm^{-1} are also reported.

Three N₂O time-resolved spectra (numbered 508, 509, 510) have been recorded (4) with natural sample pressures respectively equal to 3.49, 70.62, 70.58 hPa (2.62, 53.0, and 52.9 Torr). The gas was inserted in the vacuum chamber. This provides, with the elimination of the parasitic atmospheric absorption, the advantage of a laser cavity filling ratio practically equal to unity. All TRFT spectra of the laser emission were recorded with 64 time samples, 1.6 μs time resolution and 32 co-additions. Unapodized spectral resolutions and recording times were respectively 0.037, 0.037, 0.007 cm^{-1} and 5, 5, and 25 minutes.

Figure 1 displays the general temporal behavior of the spectrum nb. 510 with restricted spectral resolution. The laser line is narrowing with increasing generation times reaching at

most 120 μs . With 7.1 km absorption path length the spectrum covers 150 cm^{-1} , approximately from 3900 to 4050 cm^{-1} . With 33.5 km absorption path length the spectral coverage is restricted to 60 cm^{-1} , from 3955 to 4005 cm^{-1} . As in Ref.(3), it has been checked that no deviation to the linear evolution versus the generation time of the peak absorbance is observed. No attempt was made to tune the Cr^{2+} : ZnSe laser.

Wavenumber scale of the spectra have been calibrated against lines from residual water vapor in the laser chamber, using (5). Line positions reported here were measured in the 3 temporal samples of spectrum 510. Their sequence number is 6, 16, 26 corresponding to the equivalent absorption paths 7, 12, 17 km. Their respective wavenumber scales were first checked to be consistent within an average of 4 10^{-4} cm^{-1} . Full width at half maximum of the N O profiles in spectrum 510 (pressure: 70.58 hPa) is of the order of 20 10^{-3} cm^{-1} , revealing as expected contribution of collisional broadening. The accuracy of the line position measurements is of the order of 10^{-3} cm^{-1} . Only well-resolved and unsaturated lines were taken into account. Line sequences detected with a Loomis-Wood program (6), were left unprocessed and are not reported in this note, when at least 15 lines were not fitting the selection criteria. Altogether, 42 bands are observed. Among them, 32 belong to $^{14}\text{N}_2^{16}\text{O}$, 4 to $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, 4 to $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, and 2 to $^{14}\text{N}_2^{18}\text{O}$. The $^{14}\text{N}_2^{16}\text{O}$ bands consist of 1 Σ - Σ , 11 Σ - Π , 2 Σ - Φ , 2 Π - Φ , 4 Π - Π , 8 Π - Δ and 4 Δ - Φ transitions. All the $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, and $^{14}\text{N}_2^{18}\text{O}$ bands are Σ - Π transitions. Practically all the observed lines are transitions between already known energy levels. Only the 13312 $^{14}\text{N}_2^{16}\text{O}$ energy level is observed for the first time. In order to appreciate the validity of our measurements, least-squares fits of individual bands were performed using the polynomial expression:

$$E(v, J) = G + BX - DX^2 + HX^3 + LX^4 \quad \text{with} \quad X = J(J+1)$$

The lower state constants were held fixed in the fits to the excellent values given in (7) and (8). Only the lines measured in our spectra were processed in the fits.

The 42 observed bands are summarized with their assignments and calculated band centers in Table 1. A full resolution small part of the temporal sample n° 6 already shown in Figure 1 is given on Figure 2 with spectral assignments of the resolved lines. In the Journal supplementary material, 3 additional tables are given. Table 2 reports for $^{14}\text{N}_2^{16}\text{O}$ the effective parameters obtained from our calculations and their corresponding values taken in (7) and (8). Table 3 reports similar results for the isotopologues $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, and $^{14}\text{N}_2^{18}\text{O}$. Table 4 is aimed to be a convenient tool. It provides in increasing order 1637 measured line positions, with their corresponding “observed – calculated” values and their isotopologue and rovibrational assignments.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

N₂O time-resolved spectrum made of 64 time-components. Only one time-component out of five is plotted, starting from time-component n° 6. On the plot, two consecutive components, at an intermediate 0.071 cm⁻¹ apodized resolution, are 8 μs from each other. This corresponds to a 2.4-kilometer increase of the equivalent absorbing path L. N₂O pressure is 70.58 hPa

Figure 2. Limited portion of the time-component n° 6 shown on Figure 1. Spectral resolution is $7.1 \times 10^{-3} \text{ cm}^{-1}$. For the sake of clarity all assignments are not given.

Table 1

N₂O bands observed in the present TRFT-ICLAS spectra between 3901 and 4050 cm⁻¹. Energy level notation is $v_1 v_2 / v_3 x$. The v_1 's and l are the usual vibrational quantum numbers. $x = 1$ or 2 stand for the usual e and f notations. Numbers in parentheses after the band center values give one standard deviation in units of the least significant digits. N is the total number of observed lines. RMS : Root Mean Square of the polynomial fit

isotop. ν_1	Transition		Band center ν_0 (cm ⁻¹)	N lines	Observed J_{max}		RMS	
	upper	lower			P	Q	R	($\times 10^4$ cm ⁻¹)
446	03111	00001	3931.247641(20)	70	25	-	64	0.4
446	40001	02001	3937.544775(17)	64	15	-	65	6
446	03311	00001	3948.28416(28)	31	27	-	51	7
446	41101	03301	3955.91156(29)	30	43	-	54	6
446	41102	03302	3955.91221(42)	30	46	-	52	7
446	41101	03101	3973.75842(18)	55	44	-	63	5
446	41102	03101	3973.75843(33)	17	-	51	-	4
446	41101	03102	3973.75850(46)	13	-	46	-	6
446	41102	03102	3973.75863(14)	65	61	-	66	5
446	14011	03301	3995.46032(27)	27	36	-	40	6
446	14212	03302	4005.71059(31)	33	51	-	37	8
446	14211	03301	4005.71088(36)	37	55	-	37	9
446	22011	11102	4007.83943(31)	21	-	47	-	6
446	22011	11101	4007.84067(27)	28	48	-	43	6
446	14011	03102	4013.30713(25)	18	-	51	-	4
446	14011	03101	4013.30735(15)	42	51	-	38	5
446	13111	02202	4023.03477(69)	16	-	31	-	6
446	13112	02202	4023.03632(22)	25	48	-	10	4
446	13112	02201	4023.03636(43)	17	-	34	-	6
446	13111	02201	4023.03638(29)	35	41	-	21	5
446	14212	03102	4023.55756(24)	31	53	-	20	5
446	14211	03101	4023.55819(15)	29	64	-	16	4
446	13112	02001	4032.64887(37)	28	-	55	-	5
446	13111	02001	4032.64889(20)	47	61	-	8	5
446	21111	10001	4034.27055(17)	46	66	-	2	5

isotop. ^{a)}	Transition		Band center ν_0 (cm ⁻¹)	N lines	Observed J_{max}			RMS ($\times 10^4$ cm ⁻¹)
	upper	lower			P	Q	R	
446	21112	10001	4034.27081(30)	19	-	56	-	5
446	12011	01101	4041.393297(50)	50	58	-	17	0.7
446	13312	02202	4044.72530(41)	27	61	-	-	6
446	13311	02201	4044.72566(30)	25	60	-	-	6
446	12211	01101	4053.694338(28)	62	26	-	59	0.7
446	12212	01102	4053.694361(20)	64	27	-	63	0.6
446	11111	00001	4061.9795930(58)	111	66	-	45	0.3
456	12011	01102	3981.33317(18)	39	-	46	-	6
456	12011	01101	3981.33378(16)	49	63	-	34	6
456	11112	00001	3998.571578(94)	47	-	64	-	6
456	11111	00001	3998.57184(23)	57	47	-	34	8
546	12011	01101	4000.35765(22)	41	43	-	29	6
546	12011	01102	4000.35946(50)	16	-	33	-	4
546	11112	00001	4022.28933(29)	38	-	66	-	7
546	11111	00001	4022.29036(16)	53	63	-	14	7
448	11111	00001	4014.33116(20)	54	62	-	10	7
448	11112	00001	4014.33169(29)	30	-	57	-	6

^{a)} Isotopologues: 446: ¹⁴N₂¹⁶O, 456: ¹⁴N¹⁵N¹⁶O, 546: ¹⁵N¹⁴N¹⁶O, 448: ¹⁴N₂¹⁸O