

## Submillimeter Wave Spectrum and Molecular Constants of N<sub>2</sub>O

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The submillimeter wave spectrum of the N<sub>2</sub>O molecule has been investigated within the 375-565 GHz frequency range with a sensitivity better than  $10^{-8}$  cm<sup>-1</sup>. The measured frequencies include 161 lines with intensities  $\gamma \gtrsim 10^{-6}$  cm<sup>-1</sup> belonging to 22 spectroscopically different species of the molecule (specifically, the ground and some excited vibrational states of the five most abundant isotopic species of the molecule in natural abundance) with a statistical and systematic error of the order of magnitude  $10^{-8}$ . Rotational and two centrifugal stretching constants could be determined for each spectroscopic species. For each isotopic species observed, we have made a general analysis of the spectrum in different vibrational states bearing in mind resonance effects. The total number of the rotational and rovibrational constants obtained exceeds 40.

### INTRODUCTION

Precise studies of rovibrational spectra of the simplest polyatomic molecules in the widest possible frequency range are now of great significance. Such measurements yield extensive sets of molecular constants and allow the investigation of a number of intramolecular interactions. The rotational and rovibrational spectra of the N<sub>2</sub>O molecule have been investigated previously both in the microwave and infrared regions (1-7). It should be noted, however, that the microwave data are not very extensive. This is due to the low intensity of the rotational spectral lines of the molecule [the dipole moment is 0.161 debye (8)], and also to the difficulties in studying the millimeter and submillimeter wave regions where a considerable part of the spectrum is situated. The largest number of data was obtained in Ref. (7), where the frequencies of 35 lines of the main isotopic species, <sup>14</sup>N<sub>2</sub><sup>16</sup>O, in the seven lowest vibrational states were measured in the range 125-303 GHz. The statistical errors with which the frequencies of the strongest lines were measured in Ref. (7) amounted to  $5 \times 10^{-8}$  and the systematic error did not exceed  $2 \times 10^{-7}$ .

Development of a submillimeter wave spectrometer with BWO sources and acoustic detection (RAD) (9) extends considerably the possibilities of microwave studies of molecular spectra. In the present paper investigations of the submillimeter wave rotational spectrum of the N<sub>2</sub>O molecule by RAD are described. The lines of the N<sub>2</sub>O rotational spectrum were observed at room temperature in the range 375-565 GHz with a sensitivity better than  $10^{-8}$  cm<sup>-1</sup>. A total of 161 lines with intensities  $\gamma \gtrsim 10^{-6}$  cm<sup>-1</sup> were measured which belong to the ground and some excited vibrational states of the five most abundant isotopic species of the molecule in natural abundance with statistical and systematic errors of the order of magnitude of  $10^{-8}$ . The effective rotational and



TABLE I  
Frequencies of <sup>14</sup>N<sub>2</sub><sup>16</sup>O Rotational Transitions<sup>a</sup>

$\nu_1, \nu_2, \nu_3$ = $\epsilon, d$	Transition J → J + 1	Meas. Freq. (kHz) $\nu_m$	Calc. Freq. (kHz) $\nu_c$	$\nu_m - \nu_c$ (kHz)	$\nu_1, \nu_2, \nu_3$ = $\epsilon, d$	Transition J → J + 1	Meas. Freq. (kHz) $\nu_m$	Calc. Freq. (kHz) $\nu_c$	$\nu_m - \nu_c$ (kHz)
0 <sup>0</sup> 0	14 - 15	376 777 753 (9)	376 777 756 (7)	- 3	0 <sup>2</sup> 0	14 - 15	377 802 535 (9)	377 802 542 (7)	- 7
	15 - 16	401 885 802 (10)	401 885 797 (5)	+ 5		15 - 16	402 982 088 (10)	402 982 079 (5)	+ 9
	16 - 17	426 991 808 (10)	426 991 810 (5)	- 2		16 - 17	428 160 189 (5)	428 160 189 (5)	+ 6
	17 - 18	452 095 670 (11)	452 095 670 (6)	0		17 - 18	453 336 775 (11)	453 336 776 (6)	- 1
	18 - 19	477 197 247 (12)	477 197 248 (6)	- 1		18 - 19	478 511 748 (6)	478 511 748 (6)	- 11
	19 - 20	502 296 423 (12)	502 296 420 (6)	+ 3		19 - 20	503 685 005 (12)	503 685 006 (6)	- 1
	20 - 21	527 393 051 (13)	527 393 057 (7)	- 6		20 - 21	528 836 462 (13)	528 836 456 (7)	+ 6
	21 - 22	552 487 036 (14)	552 487 033 (12)	+ 3		21 - 22	554 025 998 (14)	554 025 999 (12)	- 1
	14 - 15	376 926 982 (9)	376 926 982 (7)	0	1 <sup>1</sup> 0	16 - 17	425 416 331 (35)	425 416 327 (30)	+ 4
	15 - 16	402 044 836 (10)	402 044 834 (5)	+ 2		17 - 18	430 427 642 (35)	430 427 628 (19)	+ 14
	16 - 17	427 160 632 (10)	427 160 633 (5)	- 1		18 - 19	475 436 623 (35)	475 436 667 (20)	- 44
	17 - 18	452 274 249 (11)	452 274 250 (6)	- 1		19 - 20	500 443 339 (35)	500 443 319 (22)	+ 20
	18 - 19	477 385 536 (12)	477 385 539 (6)	- 3		20 - 21	525 447 475 (35)	525 447 459 (20)	+ 16
	19 - 20	502 494 433 (12)	502 494 431 (6)	+ 2		21 - 22	550 448 930 (35)	550 448 960 (33)	- 10
	20 - 21	527 600 741 (13)	527 600 738 (7)	+ 3		16 - 17	426 343 955 (35)	426 343 951 (30)	+ 4
	21 - 22	552 704 352 (14)	552 704 356 (12)	- 2		17 - 18	451 410 036 (35)	451 410 049 (19)	+ 7
	14 - 15	377 638 917 (9)	377 638 902 (7)	+ 15		18 - 19	476 473 886 (35)	476 473 919 (20)	- 33
	15 - 16	402 804 126 (10)	402 804 123 (5)	+ 3		19 - 20	501 535 464 (35)	501 535 435 (22)	+ 29
0 <sup>1</sup> 0	16 - 17	427 967 310 (10)	427 967 319 (5)	- 9	0 <sup>3</sup> 0	20 - 21	526 594 468 (35)	526 594 471 (20)	- 3
	17 - 18	453 128 301 (11)	453 128 303 (6)	- 2		21 - 22	551 630 897 (35)	551 630 900 (33)	- 3
	18 - 19	478 286 972 (12)	478 286 968 (6)	+ 4		14 - 15	377 279 303 (35)	377 279 307 (27)	- 4
	19 - 20	503 443 198 (12)	503 443 186 (6)	+ 12		15 - 16	402 416 703 (35)	402 416 708 (19)	- 5
	20 - 21	528 596 839 (13)	528 596 831 (7)	+ 8		16 - 17	427 553 755 (35)	427 553 763 (16)	- 8
	21 - 22	553 747 764 (14)	553 747 776 (12)	- 12		17 - 18	452 833 192 (35)	452 833 204 (16)	- 12
	15 - 16	400 203 009 (10)	400 203 017 (8)	- 8		18 - 19	477 831 945 (35)	477 831 943 (16)	+ 2
	16 - 17	425 204 112 (10)	425 204 105 (6)	+ 7		19 - 20	502 940 827 (35)	502 940 823 (19)	+ 4
	17 - 18	450 203 085 (11)	450 203 072 (7)	+ 13		20 - 21	528 076 700 (35)	528 076 700 (19)	+ 6
	18 - 19	475 199 801 (12)	475 199 818 (7)	- 17		21 - 22	553 199 423 (35)	553 199 423 (31)	- 4
1 <sup>0</sup> 0	19 - 20	500 984 706 (13)	500 984 703 (7)	+ 3	0 <sup>2</sup> 0	14 - 15	378 273 248 (35)	378 273 248 (32)	- 22
	20 - 21	525 186 106 (13)	525 186 118 (7)	- 12		15 - 16	403 368 753 (35)	403 368 702 (18)	+ 51
	21 - 22	550 175 406 (14)	550 175 404 (12)	+ 2		16 - 17	453 893 533 (35)	453 893 498 (18)	+ 35
	14 - 15	377 566 687 (9)	377 566 670 (7)	+ 17		17 - 18	479 096 157 (35)	479 096 175 (19)	- 18
	15 - 16	402 723 170 (10)	402 723 138 (5)	+ 32		18 - 19	504 296 581 (35)	504 296 606 (19)	- 25
	16 - 17	427 876 776 (10)	427 876 750 (5)	+ 26		19 - 20	529 434 653 (35)	529 434 662 (19)	- 9
	17 - 18	453 027 424 (11)	453 027 450 (6)	- 26		20 - 21	554 690 231 (35)	554 690 216 (31)	+ 15
	18 - 19	478 176 176 (12)	478 176 166 (6)	+ 10		14 - 15	378 620 731 (35)	378 620 776 (27)	- 45
	19 - 20	503 319 165 (12)	503 319 166 (6)	- 1		15 - 16	403 869 228 (35)	403 869 228 (19)	+ 35
	20 - 21	528 459 840 (13)	528 459 837 (7)	+ 3		16 - 17	459 075 216 (35)	459 075 168 (16)	+ 48
	21 - 22	553 596 860 (14)	553 596 870 (12)	- 10	0 <sup>2</sup> 0	17 - 18	474 298 479 (35)	474 298 439 (17)	+ 60
2 <sup>0</sup> 0	14 - 15	377 778 561 (9)	377 778 540 (7)	+ 21		18 - 19	479 518 847 (35)	479 518 880 (19)	- 33
	15 - 16	403 932 967 (10)	403 932 971 (5)	- 4		19 - 20	504 736 336 (35)	504 736 332 (19)	+ 4
	16 - 17	429 132 318 (10)	429 132 312 (5)	+ 6		20 - 21	529 930 638 (35)	529 930 633 (19)	+ 5
	17 - 18	453 295 438 (11)	453 295 431 (6)	+ 7		21 - 22	555 161 627 (35)	555 161 622 (31)	+ 5
	18 - 19	478 463 193 (12)	478 463 189 (6)	+ 4					
	19 - 20	503 628 487 (12)	503 628 484 (6)	+ 3					
	20 - 21	528 791 162 (13)	528 791 158 (7)	+ 4					
	21 - 22	553 951 086 (14)	553 951 089 (13)	- 3					
2 <sup>2</sup> 0	14 - 15	377 778 561 (9)	377 778 540 (7)	+ 21	0 <sup>2</sup> 0	14 - 15	378 620 731 (35)	378 620 776 (27)	- 45
	15 - 16	403 932 967 (10)	403 932 971 (5)	- 4		15 - 16	403 869 228 (35)	403 869 228 (19)	+ 35
	16 - 17	429 132 318 (10)	429 132 312 (5)	+ 6		16 - 17	459 075 216 (35)	459 075 168 (16)	+ 48
	17 - 18	453 295 438 (11)	453 295 431 (6)	+ 7		17 - 18	474 298 479 (35)	474 298 439 (17)	+ 60
	18 - 19	478 463 193 (12)	478 463 189 (6)	+ 4		18 - 19	479 518 847 (35)	479 518 880 (19)	- 33
	19 - 20	503 628 487 (12)	503 628 484 (6)	+ 3		19 - 20	504 736 336 (35)	504 736 332 (19)	+ 4
	20 - 21	528 791 162 (13)	528 791 158 (7)	+ 4		20 - 21	529 930 638 (35)	529 930 633 (19)	+ 5
	21 - 22	553 951 086 (14)	553 951 089 (13)	- 3		21 - 22	555 161 627 (35)	555 161 622 (31)	+ 5

<sup>a</sup> The calculated frequencies were obtained using Eq. (1) and the constants listed in Table VI.

TABLE II  
Frequencies of  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  Rotational Transitions<sup>a</sup>

$v_1 v_2 \begin{smallmatrix}  k  \\ \tau \end{smallmatrix} \tau_{v_3}$ $\tau = c, d$	Transition $J \rightarrow J + 1$	Meas. Freq. (kHz)		Calc. Freq. (kHz)		$\nu_m - \nu_c$ (kHz)
		$\nu_m$	( $\nu_m$ )	$\nu_c$	( $\nu_c$ )	
$00^0_0$	15 - 16	388 313 736	(9)	388 313 748	(7)	- 12
	16 - 17	412 572 385	(10)	412 572 364	(5)	+ 21
	17 - 18	436 828 978	(10)	436 828 979	(5)	- 1
	18 - 19	461 083 472	(11)	461 083 474	(6)	- 2
	19 - 20	485 335 729	(12)	485 335 729	(6)	0
	20 - 21	509 585 619	(12)	509 585 627	(6)	- 8
	21 - 22	533 833 046	(13)	533 833 047	(7)	- 1
	22 - 23	558 077 877	(14)	558 077 872	(12)	+ 5
$01^{1c}_0$	16 - 17	412 754 664	(35)	412 754 653	(29)	+ 11
	17 - 18	437 021 775	(35)	437 021 830	(19)	- 55
	18 - 19	461 286 927	(35)	461 286 863	(17)	+ 64
	19 - 20	485 549 636	(35)	485 549 631	(20)	+ 5
	20 - 21	509 809 983	(35)	509 810 015	(20)	- 32
	21 - 22	534 067 894	(35)	534 067 895	(19)	- 1
	22 - 23	558 323 158	(35)	558 323 151	(32)	+ 7
$01^{1d}_0$	16 - 17	413 512 003	(35)	413 511 997	(29)	+ 6
	17 - 18	437 823 654	(35)	437 823 665	(19)	- 11
	18 - 19	462 133 172	(35)	462 133 173	(17)	- 1
	19 - 20	486 440 411	(35)	486 440 401	(20)	+ 10
	20 - 21	510 745 225	(35)	510 745 226	(20)	- 1
	21 - 22	535 047 522	(35)	535 047 527	(19)	- 5
	22 - 23	559 347 184	(35)	559 347 182	(32)	+ 2

<sup>a</sup> The calculated frequencies were obtained using Eq. (1) and the constants listed in Table VI.

stabilized BWO. A harmonic of the reference oscillator in the submillimeter wave region is provided by a frequency multiplication chain with a lock-in AFC at all multiplication stages. The frequency of the reference oscillator and thus of the submillimeter wave BWO was modulated at 180 Hz and slowly scanned. The extent of the submillimeter wave BWO frequency modulation is chosen to be less than the spectral linewidth, so

TABLE III  
Frequencies of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  Rotational Transitions<sup>a</sup>

$v_1 v_2 \begin{smallmatrix}  k  \\ \tau \end{smallmatrix} \tau_{v_3}$ $\tau = c, d$	Transition $J \rightarrow J + 1$	Meas. Freq. (kHz)		Calc. Freq. (kHz)		$\nu_m - \nu_c$ (kHz)
		$\nu_m$	( $\nu_m$ )	$\nu_c$	( $\nu_c$ )	
$00^0_0$	14 - 15	376 750 762	(9)	376 750 773	(7)	- 11
	15 - 16	401 857 048	(10)	401 857 028	(5)	+ 20
	16 - 17	426 961 257	(10)	426 961 256	(5)	+ 1
	17 - 18	452 063 322	(11)	452 063 329	(6)	- 7
	18 - 19	477 163 120	(12)	477 163 121	(6)	- 1
	19 - 20	502 260 498	(12)	502 260 504	(6)	- 6
	20 - 21	527 355 356	(13)	527 355 350	(7)	+ 6
	21 - 22	552 447 533	(14)	552 447 533	(12)	0
$01^{1c}_0$	15 - 16	401 977 590	(35)	401 977 594	(33)	- 4
	17 - 18	452 198 710	(35)	452 198 686	(20)	+ 24
	18 - 19	477 305 799	(35)	477 305 828	(21)	- 29
	19 - 20	502 410 529	(35)	502 410 526	(20)	+ 3
	20 - 21	527 512 660	(35)	527 512 649	(20)	+ 11
	21 - 22	552 612 059	(35)	552 612 064	(32)	- 5
$01^{1d}_0$	14 - 15	377 592 022	(35)	377 592 041	(27)	- 19
	15 - 16	402 754 200	(35)	402 754 186	(19)	+ 14
	16 - 17	427 914 282	(35)	427 914 268	(16)	+ 14
	17 - 18	453 072 147	(35)	453 072 157	(17)	- 10
	18 - 19	478 227 737	(35)	478 227 726	(19)	+ 11
	19 - 20	503 380 850	(35)	503 380 844	(19)	+ 6
	20 - 21	528 531 346	(35)	528 531 383	(19)	- 37
	21 - 22	553 679 232	(35)	553 679 213	(31)	+ 19

<sup>a</sup> The calculated frequencies were obtained using Eq. (1) and the constants listed in Table VI.

TABLE IV  
Frequencies of <sup>14</sup>N<sub>2</sub><sup>18</sup>O Rotational Transitions<sup>a</sup>

$\nu_1 \nu_2 \begin{smallmatrix}  x  \\ \tau \end{smallmatrix} \nu_3$ $\tau = c, d$	Transition $J \rightarrow J + 1$	Meas. Freq. (kHz)		Calc. Freq. (kHz)		$\nu_m - \nu_c$ (kHz)
		$\nu_m$	$(\Delta\nu_m)$	$\nu_c$	$(\Delta\nu_c)$	
00 <sup>0</sup> 0	15 - 16	379 413 968 ( 9)		379 413 984 ( 7)		- 16
	16 - 17	403 116 747 (10)		403 116 728 ( 5)		+ 19
	17 - 18	426 817 545 (10)		426 817 536 ( 5)		+ 9
	18 - 19	450 516 295 (11)		450 516 293 ( 6)		+ 2
	19 - 20	474 212 870 (12)		474 212 885 ( 6)		- 15
	20 - 21	497 907 195 (12)		497 907 197 ( 6)		- 2
	21 - 22	521 599 106 (13)		521 599 112 ( 7)		- 6
	22 - 23	545 288 526 (14)		545 288 517 (12)		+ 9
01 <sup>1</sup> c0	16 - 17	403 300 584 (35)		403 300 584 (33)		0
	18 - 19	450 721 500 (35)		450 721 490 (19)		+ 10
	19 - 20	474 428 692 (35)		474 428 713 (21)		- 21
	20 - 21	498 133 635 (35)		498 133 625 (20)		+ 10
	21 - 22	521 836 114 (35)		521 836 110 (19)		+ 4
	22 - 23	545 536 046 (35)		545 536 049 (32)		- 3
01 <sup>1</sup> d0	17 - 18	427 779 831 (35)		427 779 830 (31)		+ 1
	18 - 19	451 531 806 (35)		451 531 785 (19)		+ 21
	19 - 20	475 281 483 (35)		475 281 545 (20)		- 62
	20 - 21	499 029 049 (35)		499 028 995 (22)		+ 54
	21 - 22	522 774 011 (35)		522 774 024 (20)		- 13
	22 - 23	546 516 516 (35)		546 516 518 (33)		- 2

<sup>a</sup> The calculated frequencies were obtained using Eq. (1) and the constants listed in Table VI.

that the signal from a line has the form of a first derivative of the lineshape. Finally, to determine an individual line frequency the reference oscillator frequency is tuned manually or by a servo-system controlled by the output RAD signal until the output RAD signal is equal to zero (this corresponds to tuning the BWO frequency to the line center). The reference oscillator frequency is then measured by a counter, and simultaneously, a second counter measures the intermediate frequency of the AFC system. The experimental values of the frequencies of the spectral lines determined in this way are listed in Tables I-V. The instrumental measurement error is proportional to the frequency and its systematic and statistical values are near  $1 \times 10^{-8}$ . This error is dominant for the transition frequencies of the main isotopic species, <sup>14</sup>N<sub>2</sub><sup>16</sup>O, in the vibrational states (00<sup>0</sup>0), (01<sup>1</sup>c0), (01<sup>1</sup>d0), (10<sup>0</sup>0), (02<sup>0</sup>0), (02<sup>2</sup>c0), (02<sup>2</sup>d0) and of the isotopic species <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O, <sup>14</sup>N<sub>2</sub><sup>18</sup>O in the vibrational state (00<sup>0</sup>0). For the frequencies of the remaining transitions, in view of the decreased signal/noise ratio, an estimated experimental uncertainty representing the inaccuracy of tuning to the line

TABLE V  
Frequencies of <sup>14</sup>N<sub>2</sub><sup>17</sup>O Rotational Transitions<sup>a</sup>

$\nu_1 \nu_2 \begin{smallmatrix}  x  \\ \tau \end{smallmatrix} \nu_3$ $\tau = c, d$	Transition $J \rightarrow J + 1$	Meas. Freq. (kHz)		Calc. Freq. (kHz)		$\nu_m - \nu_c$ (kHz)
		$\nu_m$	$(\Delta\nu_m)$	$\nu_c$	$(\Delta\nu_c)$	
00 <sup>0</sup> 0	16 - 17	414 420 396 (35)		414 420 406 (29)		- 10
	17 - 18	438 785 508 (35)		438 785 501 (19)		+ 7
	18 - 19	463 148 448 (35)		463 148 440 (17)		+ 8
	19 - 20	487 509 107 (35)		487 509 101 (20)		+ 6
	20 - 21	511 867 356 (35)		511 867 366 (20)		- 10
	21 - 22	536 223 104 (35)		536 223 112 (19)		- 8
	22 - 23	560 576 228 (35)		560 576 221 (32)		+ 7

<sup>a</sup> The calculated frequencies were obtained using Eq. (1) and the constants listed in Table VI.

TABLE VI  
Effective Rotational and Centrifugal Stretching Constants Obtained for N<sub>2</sub>O<sup>a</sup>

Isotopic specie	$v_1 v_2 \begin{smallmatrix}  r  \\ - \\ = c, d \end{smallmatrix} v_3$	$B^{\text{eff}}$ (MHz)	$D^{\text{eff}}$ (kHz)	$H^{\text{eff}}$ (Hz)
<sup>14</sup> N <sub>2</sub> <sup>16</sup> O	00 <sup>0</sup> <sub>0</sub>	12 561.6348 (21)	5.2808 (61)	+ 0.0008 (57)
	01 <sup>1</sup> <sub>c0</sub>	12 566.6411 (21)	5.3539 (61)	+ 0.0057 (57)
	01 <sup>1</sup> <sub>d0</sub>	12 590.3906 (21)	5.4002 (61)	+ 0.0197 (57)
	10 <sup>0</sup> <sub>0</sub>	12 508.9923 (31)	5.1726 (86)	+ 0.0018 (77)
	02 <sup>0</sup> <sub>0</sub>	12 588.8913 (21)	7.4403 (61)	+ 0.0825 (57)
	02 <sup>2</sup> <sub>d0</sub>	12 595.0692 (21)	5.4482 (61)	+ 0.0029 (57)
	02 <sup>2</sup> <sub>c0</sub>	12 595.0614 (21)	3.6281 (61)	- 0.0702 (57)
	11 <sup>1</sup> <sub>c0</sub>	12 515.270 (15)	5.233 (38)	- 0.001 (33)
	11 <sup>1</sup> <sub>d0</sub>	12 542.493 (15)	5.120 (38)	- 0.023 (33)
	03 <sup>1</sup> <sub>c0</sub>	12 578.8241 (68)	6.340 (19)	+ 0.039 (18)
	03 <sup>3</sup> <sub>0</sub>	12 611.2577 (72)	4.742 (20)	- 0.102 (18)
	03 <sup>1</sup> <sub>d0</sub>	12 623.6200 (68)	6.494 (19)	- 0.035 (18)
<sup>15</sup> N <sup>14</sup> N <sup>16</sup> O	00 <sup>0</sup> <sub>0</sub>	12 137.3103 (22)	4.8896 (57)	- 0.0113 (49)
	01 <sup>1</sup> <sub>c0</sub>	12 142.711 (10)	4.960 (25)	- 0.004 (20)
	01 <sup>1</sup> <sub>d0</sub>	12 164.996 (10)	4.972 (25)	- 0.016 (20)
<sup>14</sup> N <sup>15</sup> N <sup>16</sup> O	00 <sup>0</sup> <sub>0</sub>	12 560.7310 (21)	5.2682 (61)	- 0.0081 (57)
	01 <sup>1</sup> <sub>c0</sub>	12 564.5298 (99)	5.319 (27)	- 0.021 (24)
	01 <sup>1</sup> <sub>d0</sub>	12 588.8168 (68)	5.368 (19)	- 0.003 (18)
<sup>14</sup> N <sub>2</sub> <sup>18</sup> O	00 <sup>0</sup> <sub>0</sub>	11 859.1097 (22)	4.7274 (57)	- 0.0119 (49)
	01 <sup>1</sup> <sub>c0</sub>	11 864.545 (10)	4.772 (25)	- 0.020 (20)
	01 <sup>1</sup> <sub>d0</sub>	11 885.913 (15)	4.857 (36)	+ 0.023 (28)
<sup>14</sup> N <sub>2</sub> <sup>17</sup> O	00 <sup>0</sup> <sub>0</sub>	12 191.719 (10)	4.987 (25)	- 0.004 (20)

<sup>a</sup> Uncertainties given in parentheses are standard errors.

center is defined by  $\sim 2\Delta\nu$  noise/signal. The factor  $\Delta\nu$  is the line half-width and is therefore constant over the whole frequency range. The upper limit to the experimental uncertainty estimated in this way is 50 kHz. Finally, the statistical errors for the cases of both the strong and weak lines were determined from the standard deviation of the fits to the frequencies.

Preliminary data reduction consisted of fitting the frequencies for each vibrational state of each isotopic species to the model

$$E_R^{\text{eff}} = B^{\text{eff}}J(J+1) - D^{\text{eff}}J^2(J+1)^2 + H^{\text{eff}}J^3(J+1)^3. \quad (1)$$

The resulting calculated values of the transition frequencies are shown in Tables I–V. The effective rotational and centrifugal stretching constants for each observed spectroscopic species of the N<sub>2</sub>O molecule are given in Table VI. The correlation coefficients between constants are

$$r_{B^{\text{eff}}, D^{\text{eff}}} = 0.99, \quad r_{B^{\text{eff}}, H^{\text{eff}}} = 1.00, \quad r_{D^{\text{eff}}, H^{\text{eff}}} = 0.98$$

and depend weakly on both the vibrational state and isotopic species. Each line was weighted according to the experimental uncertainty.<sup>2</sup> The standard deviations of the fits were then used to scale the original errors (10). The uncertainties quoted for the

<sup>2</sup> Method described in detail in Ref. (9).

observed frequencies in Tables I-V are those corrected uncertainties. The quoted errors following the calculated frequencies correspond to the standard deviation, i.e., 68% confidence interval. It should be noted that attempts to process simultaneously the data obtained in Ref. (7) and in this work led to a significantly poorer spectrum fit. The cause may be that the value of the systematic error in Ref. (7) is too large relative to the estimated random experimental error used.

### THEORY

To process simultaneously all experimental data obtained for each isotopic species observed, it is necessary to consider contributions to the rovibrational energy including both nonresonant and resonant vibration-rotation interactions. Our derivation of the energy eigenvalues is based on Refs. (1, 11-14).

1. The rotation-vibration energy terms of a linear molecule, obtained by the contact transformation method, are represented as

$$E_{RV}^0 = E_V^0 + E_R^0$$

$$E_V^0 = \sum_n \omega_n \left( v_n + \frac{d_n}{2} \right) + \sum_{n,m} x_{nm} \left( v_n + \frac{d_n}{2} \right) \left( v_m + \frac{d_m}{2} \right) + \sum_{t,t'} g_{t_t t_{t'}} l_t l_{t'}, \quad (2)$$

$$E_R^0 = B_v [J(J+1) - l^2] - D_v [J(J+1) - l^2]^2 + H_v [J(J+1) - l^2]^3,$$

where

$$B_v = B_e - \sum_n \alpha_n \left( v_n + \frac{d_n}{2} \right) + \sum_{n,m} \gamma_{nm} \left( v_n + \frac{d_n}{2} \right) \left( v_m + \frac{d_m}{2} \right) + \sum_{t,t'} \gamma_{t_t t_{t'}} l_t l_{t'},$$

$$D_v = D_e - \sum_n \beta_n \left( v_n + \frac{d_n}{2} \right), \quad (3)$$

$$H_v = H_e.$$

Here:

$\omega_n$	Frequency of the $n$ th normal vibration
$d_n$	Degeneracy of the $n$ th normal vibration
$v_n$	Vibrational quantum number of the $n$ th normal vibration
$x_{nm}$	Anharmonicity constants
$g_{t_t t_{t'}}$	Anharmonicity constants describing a contribution of the vibrational angular momentum to the vibrational energy: $t$ and $t'$ are the indices of degenerate bending vibrations
$l_t$	Quantum number of vibrational angular momentum corresponding to the $t$ th degenerate bending mode; $l = \sum_t l_t$
$B_e, D_e, H_e$	Rotational and centrifugal stretching constants for equilibrium configuration
$B_v, D_v, H_v$	Rotational and centrifugal stretching constants in the vibrational state
$\alpha_n, \gamma_{nm}$ $\gamma_{t_t t_{t'}}$	Rotation-vibration interaction constants

TABLE VII

Rotation-Vibration Energy Matrices for the (01<sup>0</sup>) and the (10<sup>0</sup>), (02<sup>0</sup>), (02<sup>2</sup>) Vibrational States

		$01^{1+0}$	$01^{1-0}$
$01^{10}$	$01^{1+0}$	$E_{+1,+1}^{010} + v_{-1,+1}^{010}$	0
	$01^{1-0}$	0	$E_{+1,+1}^{010} - v_{-1,+1}^{010}$

  

		$10^{0+0}$	$02^{0+0}$	$02^{2+0}$
$10^{00}$ $02^{00}$ $02^{20}$	$10^{0+0}$	$E_{0,0}^{100}$	$v_F^{100}$	0
	$02^{0+0}$	$v_F^{100}$	$E_{0,0}^{020}$	$\sqrt{2} v_{0,+2}^{020}$
	$02^{2+0}$	0	$\sqrt{2} v_{0,+2}^{020}$	$E_{+2,+2}^{020} + v_{-2,+2}^{020}$
	$02^{2-0}$			
		$02^{2-0}$	$E_{+2,+2}^{020} - v_{-2,+2}^{020}$	

There are three vibrations in the N<sub>2</sub>O molecule, including one bending mode. In standard notation  $v = (v_1 v_2^{ll} v_3)$  and for the main isotopic species, <sup>14</sup>N<sub>2</sub><sup>16</sup>O,  $E(01^0) = 588.78 \text{ cm}^{-1}$ ,  $E(10^0) = 1284.91 \text{ cm}^{-1}$ , and  $E(00^01) = 2223.76 \text{ cm}^{-1}$  (1). There remains only one term in the sums over the indices  $l$  and  $l'$ .

The contact transformation method used to obtain expressions (2) and (3) is the perturbation theory method. Therefore, it is inapplicable in those cases when the difference between the energies of two (or more) interacting levels in the initial basis is either equal to zero in the zero-order approximation or has the same order of magnitude as the energy of coupling of these levels. This interaction between similar levels is called resonance. The resonant levels are grouped in separate irreducible blocks which can be diagonalized to obtain the eigenvalues and eigenfunctions. To describe the lowest vibrational states of the N<sub>2</sub>O molecule, one has to take into account the following two types of resonances (1).

#### A. *l*-type resonance

$$\langle v_1 v_2^l v_3 J | | v_1 v_2^{l \pm 2} v_3 J \rangle = \frac{1}{2} q \{ (v_2 \mp l)(v_2 \pm l + 2)[J(J+1) - l(l \pm 1)][J(J+1) - (l \pm 1)(l \pm 2)] \}^{\frac{1}{2}}, \quad (4)$$

$$q = q_v + q_J \cdot J(J+1) + q_{JJ} J^2(J+1)^2, \quad (5)$$

$$q_v = q_{(010)} + q_1 v_1 + q_2 (v_2 - 1) + q_3 v_3,$$

where  $q$  is the second-order  $l$ -doubling constant. The values  $q_J$ ,  $q_{JJ}$ ,  $q_1$ ,  $q_2$ ,  $q_3$  define a weak dependence of the  $l$ -type doubling constants on the rovibrational state.

It should be noted that in paper (13) matrix elements of the type  $\langle v_1 v_2^l v_3 J | | v_1 v_2^{l \pm 4} v_3 J \rangle$  were introduced for processing the precise microwave measurements of HCN and DCN spectra. For the relevant values of  $v_2$  one may write

$$\begin{aligned} \langle v_1 2^{-2} v_3 J | | v_1 2^2 v_3 J \rangle &= 2\rho \{ J(J+1)[J(J+1) - 2] \}, \\ \langle v_1 3^{-1} v_3 J | | v_1 3^3 v_3 J \rangle &= 2\rho J(J+1) \{ 3[J(J+1) - 2][J(J+1) - 6] \}^{\frac{1}{2}}, \end{aligned} \quad (6)$$

where  $\rho$  is the fourth-order  $l$ -doubling constant.



## B. Fermi resonance

$$\langle v_1 v_2 {}^l v_3 J | v_1 - 1 (v_2 + 2) {}^l v_3 J \rangle = -\frac{K^{122}}{2} \left\{ \frac{v_1}{2} [(v_2 + 2)^2 - l^2] \right\}^{\frac{1}{2}}, \quad (7)$$

$$K^{122} = K_v^{122} + \lambda_J J(J+1), \quad (8)$$

$$K_v^{122} = K_{(100)}^{122} + \lambda_1(v_1 - 1) + \lambda_2 v_2 + \lambda_3 v_3.$$

Here  $K^{122}$  is the coefficient of the term  $q_1(q_{21}^2 + q_{22}^2)$  in the normal-coordinate series expansion of the potential energy, where the  $q$ 's represent normal coordinates.

2. Let us consider the energies of specific rovibrational states of interest taking into account resonance interactions. The initial energy levels specified by Eq. (2) may then be grouped in irreducible blocks.

A. The ground vibrational state (00<sup>0</sup>0)

$$E_{(00^0 0)} = E_0, \\ E_R = B_0 J(J+1) - D_0 J^2(J+1)^2 + H_0 J^3(J+1)^3.$$

Here  $E_0$ ,  $B_0$ ,  $D_0$ , and  $H_0$  are the vibrational energy, rotational and centrifugal stretching constants in the ground vibrational state.

B. Excited vibrational state (01<sup>1</sup>0). The two vibrational components of this state are coupled by  $l$ -type resonance. The resulting energy matrix in the basis symmetrized with respect to  $l$ ,

$$|v_1 v_2 {}^{l\pm} v_3 J\rangle = (1/\sqrt{2}) [|v_1 v_2 {}^{+l} v_3 J\rangle \pm |v_1 v_2 {}^{-l} v_3 J\rangle], \quad l \neq 0, \\ |v_1 v_2 {}^{0+} v_3 J\rangle = |v_1 v_2 {}^0 v_3 J\rangle,$$

is given in Table VII and the form of the matrix elements in Table IX.

C. Excited vibrational states (10<sup>0</sup>0), (02<sup>0</sup>0), (02<sup>2</sup>0). These states are coupled by  $l$ -type and Fermi resonances. The energy matrix in the symmetrized basis is shown in Table VII and the form of the matrix elements in Table IX.

TABLE VIII

Rotation-Vibration Energy Matrices for the (11<sup>1</sup>0), (03<sup>1</sup>0), (03<sup>3</sup>0) Vibrational States

		11 <sup>1+</sup> 0	03 <sup>1+</sup> 0	03 <sup>3+</sup> 0
11 <sup>1</sup> 0	11 <sup>1+</sup> 0	$E_{+1,+1}^{110} + v_{-1,+1}^{110}$	$v_F^{110}$	0
	03 <sup>1+</sup> 0	$v_F^{110}$	$E_{+1,+1}^{030} + v_{-1,+1}^{030}$	$v_{+1,+3}^{030} + v_{-1,+3}^{030}$
	03 <sup>3+</sup> 0	0	$v_{+1,+3}^{030} + v_{-1,+3}^{030}$	$E_{+3,+3}^{030}$
03 <sup>1</sup> 0		11 <sup>1-</sup> 0	03 <sup>1-</sup> 0	03 <sup>3-</sup> 0
03 <sup>3</sup> 0	11 <sup>1-</sup> 0	$E_{+1,+1}^{110} - v_{-1,+1}^{110}$	$v_F^{110}$	0
	03 <sup>1-</sup> 0	$v_F^{110}$	$E_{+1,+1}^{030} - v_{-1,+1}^{030}$	$v_{+1,+3}^{030} - v_{-1,+3}^{030}$
	03 <sup>3-</sup> 0	0	$v_{+1,+3}^{030} - v_{-1,+3}^{030}$	$E_{+3,+3}^{030}$

TABLE IX

Matrix Elements of Rotation-Vibration Energy Matrices Given in Tables VII and VIII

$(01^1 0)$	$E_{+1,+1}^{010} = E_{(010)}^0 + B_{\tau} + [B_{(010)} + v_{\tau} J(J+1) - 1] + D_{(010)} J(J+1) - 1 + H_{(010)} J(J+1)^3$ $V_{-1,\tau+1}^{010} = -q_{(010)} + q_J J(J+1) + q_{JJ} J^2(J+1)^2 - J(J+1)$
$(10^0 0)$ $(02^0 0)$ $(02^2 0)$	$E_{0,0}^{100} = E_{(100)}^0 + B_{(100)} J(J+1) - B_{(100)} J^2(J+1)^2 + H_{(100)} J^3(J+1)^3$ $E_{0,0}^{020} = E_{(020)}^0 + B_{(020)} J(J+1) - B_{(020)} J^2(J+1)^2 + H_{(020)} J^3(J+1)^3$ $E_{+2,+2}^{020} = E_{(020)}^0 + 4B_{\tau} + [B_{(020)} + 4v_{\tau} J(J+1) - 4] - D_{(020)} [J(J+1) + 4] + H_{(020)} [J(J+1) - 4]^3$ $V_F^{100} = -[K_{(100)}^{122} + \lambda_J J(J+1)] \cdot 1/\sqrt{2}$ $V_{0,+2}^{020} = [q_{(020)} + q_J J(J+1) + q_{JJ} J^2(J+1)^2] \{2J(J+1) - J(J+1) - 2\}^{1/2}$ $V_{-2,+2}^{020} = 2q_J J(J+1) [J(J+1) - 2]$
$(11^1 0)$ $(03^1 0)$ $(03^3 0)$	$E_{+1,+1}^{110} = E_{(110)}^0 + B_{\tau} + [B_{(110)} + v_{\tau} J(J+1) - 1] - D_{(110)} J(J+1) - 1 + H_{(110)} [J(J+1) - 1]^3$ $E_{+3,+3}^{030} = E_{(030)}^0 + 9B_{\tau} + [B_{(030)} + 9v_{\tau} J(J+1) - 9] - D_{(030)} [J(J+1) - 9] + H_{(030)} [J(J+1) - 9]^3$ $E_{+1,+1}^{030} = E_{(030)}^0 + B_{\tau} + [B_{(030)} + v_{\tau} J(J+1) - 1] - D_{(030)} [J(J+1) - 1] + H_{(030)} [J(J+1) - 1]^3$ $V_F^{110} = -[K_{(110)}^{122} + \lambda_J J(J+1)]$ $V_{-1,+1}^{110} = -q_{(110)} + q_J J(J+1) + q_{JJ} J^2(J+1)^2 - J(J+1)$ $V_{-1,+1}^{030} = 2[q_{(030)} + q_J J(J+1) + q_{JJ} J^2(J+1)^2] - J(J+1)$ $V_{+1,+3}^{030} = -q_{(030)} + q_J J(J+1) + q_{JJ} J^2(J+1)^2 \{3[J(J+1) - 2][J(J+1) - 6]\}^{1/2}$ $V_{-1,+3}^{030} = 2p_J J(J+1) \{3[J(J+1) - 2][J(J+1) - 6]\}^{1/2}$

D. *Excited vibrational states* ( $11^1 0$ ), ( $03^1 0$ ), ( $03^3 0$ ). The six vibrational components within this group of states are coupled by  $l$ -type and Fermi resonances. The energy matrix is the symmetrized basis is presented in Table VIII and the matrix elements are given in Table IX.

#### DETERMINATION OF THE MOLECULAR CONSTANTS OF $N_2O$

The molecular constants of  $N_2O$  were found for each isotopic species of the molecule by processing all experimental data referring to different vibrational states in the framework of the linear molecular model, bearing in mind both resonance and nonresonance interactions. The most complete set of constants has been obtained for the main isotopic species  $^{14}N_2^{16}O$  for which there are available numerous experimental data.

1. Let us define the independent molecular constants or their combinations sufficient to describe the experimental data. For describing with the necessary accuracy the pure rotational spectrum in the absence of resonance effects, one may choose the set of constants  $B_0$ ,  $D_0$ , and  $H_0$ , the rotational and centrifugal constants of the ground vibrational state;  $\alpha_n$  (three constants),  $\gamma_{nm}$  (six constants),  $\gamma_{ll}$ , and  $\beta_n$  (three constants), the constants of nonresonant rotation-vibration interaction. However, experimental data on the main isotopic species,  $^{14}N_2^{16}O$ , are available only for states in which

$$v_1^2 = v_1 \quad \text{and} \quad v_3 = 0, \quad (9)$$

TABLE X  
Molecular Constants of <sup>14</sup>N<sub>2</sub> <sup>16</sup>O as Defined by Eqs. (2)–(8)<sup>a</sup>

	A	B	C
$B_0$	12 561.6365 (9)	12 561.6370 (9)	12 561.6369 (9)
$\alpha_1$	59.93 (76)	58.786 (69)	58.78678 (86)
$\alpha_2$	- 17.03758 (94)	- 17.03656 (55)	- 17.03655 (35)
$\gamma_{12}$ MHz	- 0.99 (38)	- 0.415 (35)	- 0.41472 (42)
$\gamma_{22}$	0.11 (19)	- 0.171 (17)	- 0.17087 (14)
$\gamma_{J J}$	- 0.29 (19)	- 0.000 (17)	0
$D_0$	5.2861 (24)	5.2869 (24)	5.2869 (24)
$\beta_1$ kHz	- 0.0484 (33)	- 0.0515 (20)	- 0.05153 (92)
$\beta_2$	- 0.08390 (77)	- 0.08303 (47)	- 0.08303 (35)
$H_0$ Hz	0.0059 (22)	0.0061 (22)	0.0061 (22)
$q_{(010)}$	11.8734 (12)	11.8734 (12)	11.87212 (27)
$q_1$ MHz	- 0.05 (23)	0.25 (39)	0.253 (23)
$q_2$	0.113 (56)	0.0377 (97)	0.0379 (56)
$q_J$	- 19.4 (36)	- 19.5 (36)	- 15.68 (38)
$q_{JJ}$ Hz	0.0034 (33)	0.0035 (33)	0
$\rho$	- 1.48 (58)	- 0.88 (33)	- 0.86 (15)
$g_{J J}$ GHz	- 8 (19)	16.8 (14)	16.79 (83)
$\angle 1$	3.48 (34)	2.960	2.9604
$\angle 2$ THz	3.45 (33)	2.936	2.9360
$k_{(100)}^{122}$	1.69 (26)	1.322 (15)	1.3221 (87)
$\lambda_2$	0.021 (22)	- 0.0124 (42)	- 0.0123 (24)
$\lambda_J$ MHz	- 2.52 (63)	- 2.58 (21)	- 2.58 (18)

<sup>a</sup> Standard errors are given in parentheses. The three analyses are: (A) Data consisted of experimental frequencies in Table I except for the (03<sup>0</sup>0) state; all parameters were varied. (B) Data as in (A), and in addition infrared data were used to fix the values of  $\Delta_1$  and  $\Delta_2$  (see text). (C) Data as in (B), and in addition the condition  $\gamma_{JJ} = 0$  was imposed.

and instead of expression (3), one may write

$$\begin{aligned}
 B_v &= B_0 - \alpha_1^* v_1 - \alpha_2^* v_2 + 2\gamma_{12} v_1 v_2 + \gamma_{22} v_2^2 + \gamma_{JJ} J^2, \\
 D_v &= D_0 - \beta_1 v_1 - \beta_2 v_2, \\
 H_v &= H_0,
 \end{aligned} \tag{10}$$

where

$$\begin{aligned}
 \alpha_1^* &= \alpha_1 - 2\gamma_{11} - 2\gamma_{12} - \gamma_{13}, \\
 \alpha_2^* &= \alpha_2 - \gamma_{12} - 2\gamma_{22} - \gamma_{23}.
 \end{aligned}$$

Thus, only seven constants,  $\alpha_1^*$ ,  $\alpha_2^*$ ,  $\gamma_{12}$ ,  $\gamma_{22}$ ,  $\gamma_{JJ}$ ,  $\beta_1$ ,  $\beta_2$ , of the nonresonant vibration-rotation interaction are independent and can be determined.

TABLE XI

Matrix of Correlation Coefficients for  $^{14}\text{N}_2^{16}\text{O}$  Molecular Constants; Case "A"

	$B_0$	$\alpha_1^*$	$\alpha_2^*$	$\gamma_{12}$	$\gamma_{22}$	$\gamma_{44}$	$\beta_0$	$\beta_1$	$\beta_2$	$\eta_0$	$q_{(010)}$
$B_0$	1										
$\alpha_1^*$	-0.29	1									
$\alpha_2^*$	+0.37	-0.65	1								
$\gamma_{12}$	+0.29	-1.00	+0.65	1							
$\gamma_{22}$	-0.29	+1.00	-0.65	-1.00	1						
$\gamma_{44}$	+0.29	-1.00	+0.65	+1.00	-1.00	1					
$\beta_0$	+0.96	-0.19	+0.19	+0.19	-0.19	+0.19	1				
$\beta_1$	-0.23	+0.57	-0.86	-0.57	+0.57	-0.57	-0.14	1			
$\beta_2$	+0.42	-0.67	+0.95	+0.67	-0.67	+0.67	+0.23	-0.80	1		
$\eta_0$	+0.86	-0.06	+0.01	+0.06	-0.06	+0.06	+0.97	-0.04	+0.02	1	
$q_{(010)}$	+0.01	-0.02	-0.00	+0.02	-0.02	+0.02	+0.00	-0.00	+0.01	+0.00	1
$q_1$	+0.29	-0.93	+0.73	+0.93	-0.93	+0.93	-0.18	-0.67	+0.73	+0.05	+0.06
$q_2$	-0.29	+0.93	-0.73	-0.93	+0.93	-0.93	-0.18	+0.67	-0.73	-0.05	-0.06
$q_J$	-0.01	+0.03	-0.00	-0.03	+0.03	-0.03	-0.01	+0.01	-0.01	-0.00	-0.99
$q_{JJ}$	+0.01	-0.03	+0.01	+0.03	-0.03	+0.03	+0.01	-0.01	+0.02	+0.00	+0.97
$\rho$	+0.25	-0.62	+0.92	+0.62	-0.62	+0.62	+0.14	-0.93	+0.86	-0.00	-0.02
$g_{44}$	+0.30	-0.98	+0.74	+0.98	-0.98	+0.98	+0.19	-0.68	+0.75	+0.06	+0.04
$\Delta_1$	-0.30	+0.99	-0.72	-0.99	+0.99	-0.99	-0.19	+0.66	-0.73	-0.06	-0.01
$\Delta_2$	-0.29	+0.99	-0.70	-0.99	+0.99	-0.99	-0.19	+0.63	-0.71	-0.06	-0.01
$K_{(100)}^{122}$	-0.30	+0.99	-0.74	-0.98	+0.98	-0.99	-0.19	+0.67	-0.74	-0.06	-0.03
$\lambda_2$	-0.29	+0.99	-0.62	-0.99	+0.99	-0.99	-0.19	+0.52	-0.65	-0.07	-0.02
$\lambda_J$	+0.07	-0.04	+0.36	+0.03	-0.04	+0.04	+0.03	-0.39	+0.32	-0.02	+0.11

	$q_1$	$q_2$	$q_J$	$q_{JJ}$	$\rho$	$g_{44}$	$\Delta_1$	$\Delta_2$	$K_{(100)}^{122}$	$\lambda_2$	$\lambda_J$
$q_1$	1										
$q_2$	-1.00	1									
$q_J$	-0.05	+0.05	1								
$q_{JJ}$	+0.05	-0.05	-0.99	1							
$\rho$	+0.71	-0.71	+0.01	-0.01	1						
$g_{44}$	+0.98	-0.98	-0.04	+0.04	+0.72	1					
$\Delta_1$	-0.93	+0.93	+0.02	-0.03	-0.70	-0.98	1				
$\Delta_2$	-0.90	+0.90	+0.02	-0.03	-0.67	-0.97	+1.00	1			
$K_{(100)}^{122}$	-0.97	+0.97	+0.03	-0.04	-0.72	-1.00	+0.99	+0.98	1		
$\lambda_2$	-0.92	+0.92	+0.03	-0.04	-0.58	-0.97	+0.98	+0.98	+0.97	1	
$\lambda_J$	+0.41	-0.41	-0.06	+0.05	+0.40	+0.24	-0.06	+0.00	-0.19	-0.04	1

The presence of resonant interactions ( $l$ -type and Fermi resonances) leads to the appearance of the constants involved in the matrix elements of the resonant interactions and in the differences between the resonant terms. Taking into account Eq. (9), one can determine the 12 independent constants of the resonant interactions,  $q_{(010)}$ ,  $q_1$ ,  $q_2$ ,  $q_J$ ,  $q_{JJ}$ , and  $\rho$ , the constants involved in the matrix elements of  $l$ -type resonance;  $g_{44}$ , the constant involved in the difference between terms coupled through  $l$ -type resonance;  $K_{(100)}^{122}$ ,  $\lambda_2$ , and  $\lambda_J$ , the constants in the matrix elements of Fermi resonance;  $\Delta_1 = E_{(100)}^0 - E_{(020)}^0$ , and  $\Delta_2 = E_{(110)}^0 - E_{(030)}^0$ , the constants giving the difference between terms coupled through Fermi resonance.

Thus, the maximum number of the constants to be determined is equal to 22.

TABLE XI

Matrix of Correlation Coefficients for <sup>14</sup>N<sub>2</sub><sup>16</sup>O Molecular Constants; Case "B"

	B <sub>0</sub>	α <sub>1</sub>	α <sub>2</sub>	γ <sub>12</sub>	γ <sub>22</sub>	γ <sub>ff</sub>	D <sub>0</sub>	β <sub>1</sub>	β <sub>2</sub>	H <sub>0</sub>	q <sub>(010)</sub>
B <sub>0</sub>	1										
α <sub>1</sub>	+ 0.07	1									
α <sub>2</sub>	+ 0.26	+ 0.77	1								
γ <sub>12</sub>	- 0.07	- 1.00	- 0.77	1							
γ <sub>22</sub>	+ 0.07	+ 1.00	+ 0.77	- 1.00	1						
γ <sub>ff</sub>	- 0.07	- 1.00	- 0.77	+ 1.00	- 1.00	1					
D <sub>0</sub>	+ 0.97	+ 0.01	+ 0.10	- 0.01	+ 0.01	- 0.01	1				
β <sub>1</sub>	- 0.03	- 0.88	- 0.63	+ 0.89	- 0.89	+ 0.89	- 0.03	1			
β <sub>2</sub>	+ 0.33	+ 0.67	+ 0.86	- 0.67	+ 0.67	- 0.67	+ 0.16	- 0.49	1		
H <sub>0</sub>	+ 0.89	- 0.04	- 0.03	+ 0.04	- 0.04	+ 0.04	+ 0.97	- 0.03	- 0.02	1	
q <sub>(010)</sub>	- 0.00	- 0.08	- 0.08	+ 0.08	- 0.08	+ 0.08	+ 0.00	+ 0.07	- 0.05	+ 0.01	1
q <sub>1</sub>	+ 0.01	- 0.82	- 0.50	+ 0.82	- 0.82	+ 0.82	+ 0.03	+ 0.70	- 0.38	+ 0.04	+ 0.08
q <sub>2</sub>	- 0.01	+ 0.82	+ 0.50	- 0.82	+ 0.82	- 0.82	- 0.03	- 0.70	+ 0.38	- 0.04	- 0.08
q <sub>J</sub>	+ 0.00	+ 0.07	+ 0.06	- 0.07	+ 0.07	- 0.07	- 0.00	- 0.06	+ 0.04	- 0.01	- 0.99
q <sub>JJ</sub>	+ 0.00	- 0.05	- 0.05	+ 0.05	- 0.05	+ 0.05	+ 0.00	+ 0.04	- 0.03	+ 0.00	+ 0.97
ρ	+ 0.06	+ 0.89	+ 0.78	- 0.89	+ 0.89	- 0.89	+ 0.01	- 0.81	+ 0.63	- 0.04	- 0.12
q <sub>ff</sub>	+ 0.01	- 0.80	- 0.47	+ 0.81	- 0.80	+ 0.80	+ 0.03	+ 0.68	- 0.37	+ 0.04	+ 0.08
K <sub>(100)</sub> <sup>122</sup>	- 0.01	+ 0.81	+ 0.49	- 0.82	+ 0.81	- 0.81	- 0.03	- 0.70	+ 0.38	- 0.04	- 0.08
λ <sub>2</sub>	- 0.01	+ 0.81	+ 0.49	- 0.81	+ 0.81	- 0.81	- 0.03	- 0.69	+ 0.37	- 0.04	- 0.08
λ <sub>J</sub>	+ 0.06	- 0.48	- 0.17	+ 0.49	- 0.48	+ 0.48	+ 0.05	+ 0.39	- 0.08	+ 0.03	+ 0.07

	q <sub>1</sub>	q <sub>2</sub>	q <sub>J</sub>	q <sub>JJ</sub>	ρ	q <sub>ff</sub>	K <sub>(100)</sub> <sup>122</sup>	λ <sub>2</sub>	λ <sub>J</sub>
q <sub>1</sub>	1								
q <sub>2</sub>	- 1.00	1							
q <sub>J</sub>	- 0.07	+ 0.07	1						
q <sub>JJ</sub>	+ 0.05	- 0.05	- 0.99	1					
ρ	- 0.65	+ 0.65	+ 0.10	- 0.08	1				
q <sub>ff</sub>	+ 1.00	- 1.00	- 0.07	+ 0.05	- 0.62	1			
K <sub>(100)</sub> <sup>122</sup>	- 1.00	+ 1.00	+ 0.07	- 0.05	+ 0.64	- 1.00	1		
λ <sub>2</sub>	- 1.00	+ 1.00	+ 0.07	- 0.05	+ 0.63	- 1.00	+ 1.00	1	
λ <sub>J</sub>	+ 0.90	- 0.90	- 0.05	+ 0.04	- 0.31	+ 0.91	- 0.90	- 0.91	1

Predicted frequencies using preliminary constants showed that the splitting between the rotational transitions for the states (03<sup>3</sup>0) and (03<sup>3</sup>d0) is of the order of 1 MHz. We did not observe this splitting in the experiment (the measured half-width of the lines was about 2 MHz) and thus the measurement error of the transition frequencies in these vibrational states may be as much as 1 MHz. Therefore the rotational transitions in the vibrational states (03<sup>3</sup>0), (03<sup>3</sup>d0) are excluded from processing. The problem of finding all 22 molecular constants simultaneously (variant "A") was solved using the remaining experimental data for the isotopic species <sup>14</sup>N<sub>2</sub><sup>16</sup>O. The resulting values of the constants, their correlation coefficient matrix, and the spectral line frequencies obtained are presented in columns A of Tables X, XI, XII, respectively. One can see that many constants are not well determined. The choice of which poorly defined constants to exclude is a complicated problem because of the large correlation coefficients between them.

TABLE XI

Matrix of Correlation Coefficients for  $^{14}\text{N}_2\ ^{16}\text{O}$  Molecular Constants; Case "B"—*Continued*

	$B_0$	$\alpha_1$	$\alpha_2$	$\gamma_{12}$	$\gamma_{22}$	$D_0$	$\rho_1$	$\rho_2$	$H_0$
$B_0$	1								
$\alpha_1$	+ 0.05	1							
$\alpha_2$	+ 0.32	+ 0.45	1						
$\gamma_{12}$	+ 0.08	- 0.00	+ 0.10	1					
$\gamma_{22}$	+ 0.06	+ 0.50	+ 0.69	- 0.08	1				
$D_0$	+ 0.97	- 0.05	+ 0.14	+ 0.05	- 0.00	1			
$\rho_1$	+ 0.06	+ 0.69	+ 0.18	- 0.12	- 0.08	- 0.05	1		
$\rho_2$	+ 0.38	+ 0.31	+ 0.72	+ 0.25	+ 0.09	+ 0.21	+ 0.31	1	
$H_0$	+ 0.90	- 0.14	+ 0.01	+ 0.02	- 0.01	+ 0.98	- 0.16	+ 0.02	1
$q_{(010)}$	+ 0.00	- 0.07	- 0.02	+ 0.05	- 0.07	+ 0.00	- 0.00	+ 0.01	+ 0.00
$q_1$	+ 0.11	+ 0.15	+ 0.35	+ 0.81	+ 0.23	+ 0.06	- 0.09	+ 0.38	+ 0.02
$q_2$	- 0.11	- 0.15	- 0.35	- 0.81	- 0.23	- 0.06	+ 0.09	- 0.38	- 0.02
$q_J$	- 0.00	+ 0.07	+ 0.02	- 0.05	+ 0.07	- 0.00	+ 0.00	- 0.01	- 0.00
$\rho$	+ 0.01	+ 0.57	+ 0.34	+ 0.09	+ 0.66	- 0.00	- 0.11	+ 0.11	- 0.02
$q_{J,J}$	+ 0.11	+ 0.16	+ 0.36	+ 0.81	+ 0.25	+ 0.06	- 0.09	+ 0.38	+ 0.02
$K_{(100)}^{122}$	- 0.11	- 0.15	- 0.35	- 0.81	- 0.23	- 0.06	+ 0.09	- 0.38	- 0.02
$\lambda_2$	- 0.11	- 0.16	- 0.35	- 0.82	- 0.23	- 0.06	+ 0.09	- 0.38	- 0.02
$\lambda_J$	+ 0.11	+ 0.15	+ 0.36	+ 0.81	+ 0.23	+ 0.06	- 0.09	+ 0.38	+ 0.02

	$q_{(010)}$	$q_1$	$q_2$	$q_J$	$\rho$	$q_{J,J}$	$K_{(100)}^{122}$	$\lambda_2$	$\lambda_J$
$q_{(010)}$	1								
$q_1$	+ 0.04	1							
$q_2$	- 0.04	- 1.00	1						
$q_J$	- 0.96	- 0.04	+ 0.03	1					
$\rho$	- 0.08	+ 0.30	- 0.30	+ 0.09	1				
$q_{J,J}$	+ 0.03	+ 1.00	- 1.00	- 0.03	+ 0.32	1			
$K_{(100)}^{122}$	- 0.04	- 1.00	+ 1.00	+ 0.04	- 0.29	- 1.00	1		
$\lambda_2$	- 0.03	- 1.00	+ 1.00	+ 0.03	- 0.30	- 1.00	+ 1.00	1	
$\lambda_J$	+ 0.04	+ 1.00	- 1.00	- 0.04	+ 0.30	+ 1.00	- 1.00	- 1.00	1

Actually, a strong correlation between two poorly defined constants testifies to the fact that they are nearly interchangeable from the point of view of the description of the available experimental data. For this reason only their combination may be determined and we do not succeed in distinguishing the contribution of each constant. An attempt to exclude one of these constants, simply setting it equal to zero, will lead only to much better accuracy of definition of the remaining constant, without appreciably worsening the spectrum fit. We cannot guarantee, however, that in this case the constants will keep their physical meanings. We simply obtain in this way a set of parameters sufficient for describing the available experimental data. To avoid this difficulty, we included infrared experimental data on the difference between the energy levels  $(10^0)$ ,  $(02^0)$ , and  $(11^{1c}, d_0)$ ,  $(03^{1c}, d_0)$  at  $J = J_{\min} = |J|$ , i.e.,

$$\Delta_1^* = E_{|10^0, J=0\rangle} - E_{|02^0, J=0\rangle},$$

$$\Delta_2^* = E_{|11^{1c}, d_0, J=0\rangle} - E_{|03^{1c}, d_0, J=0\rangle}.$$

According to Ref. (1),

$$\Delta_1^* = 116.773 \text{ cm}^{-1} = 3.50077 \text{ THz},$$

$$\Delta_2^* = 131.210 \text{ cm}^{-1} = 3.93358 \text{ THz}.$$

The accuracy of determination of these values is considerably higher than is necessary for our purposes, since these constants are used only in perturbation terms affecting the rotational spectrum. It is easy to obtain the relations between  $\Delta_1^*$  and  $\Delta_2^*$  and the unperturbed differences  $\Delta_1$  and  $\Delta_2$  according to

$$\begin{aligned} \Delta_1 &= \{(\Delta_1^*)^2 - 2[K_{(100)}^{122}]^2\}^{\frac{1}{2}}, \\ \Delta_2 &= \{(\Delta_2^*)^2 - 4[K_{(100)}^{122} + \lambda_2]^2\}^{\frac{1}{2}} + \alpha_1 - 2\alpha_2. \end{aligned} \quad (11)$$

The molecular constants were determined holding  $\Delta_1$  and  $\Delta_2$  fixed at the values determined using Eq. (11). This calculation was repeated, inserting the new values of  $K_{(100)}^{122}$ ,  $\lambda_2$ ,  $\alpha_1$ , and  $\alpha_2$  until the changes in these constants were no greater than their standard error. The results of this variant are presented as case B of Tables X, XI, and XII.

Now that the determination of the molecular constants has been improved we considered the possibility of excluding some of the constants which are not essential for describing the available experimental data.  $\gamma_{ll}$  and  $q_{JJ}$  are the most poorly defined constants. Since they correlate only weakly with each other ( $r_{\gamma_{ll}, q_{JJ}} = +0.05$ ), the conditions of their exclusion may be considered independently. The fit of the spectrum under the condition  $\gamma_{ll} = q_{JJ} = 0$  is essentially unchanged. However, this is only a necessary, not a sufficient, condition for omitting these constants. From part B of Table XI it is seen that the constant  $q_{JJ}$  is strongly correlated with the constants  $q_{(010)}$  and  $q_J$ , which, then, are the only constants that will be significantly refined when the condition  $q_{JJ} = 0$  is imposed. These constants appear in the description of the spectrum in the combination

$$q_{(010)} + q_J J(J+1) + q_{JJ} J^2(J+1)^2.$$

If it is desirable to keep the physical meaning of the molecular constants as determined by Eqs. (2)–(8), the constant  $q_{JJ}$  may be neglected only in the case when

$$|q_{JJ}| J^2(J+1)^2 \lesssim \{[\overline{q_{(010)}} - \bar{q}_{(010)}) - (q_J - \bar{q}_J)J(J+1)]^2\}^{\frac{1}{2}}, \quad (12)$$

where the barred and unbarred values of  $q_{(010)}$  and  $q_J$  are calculated with and without requiring  $q_{JJ} = 0$ , respectively. Analogous arguments lead to the following estimation for the constant  $\gamma_{ll}$ .

$$|\gamma_{ll}| l^2 \leq \{[(\alpha_1^* - \bar{\alpha}_1^*)v_1 + 2(\gamma_{12} - \bar{\gamma}_{12})v_1v_2 + (\gamma_{22} - \bar{\gamma}_{22})v_2^2]^2\}^{\frac{1}{2}}. \quad (13)$$

The results obtained with  $q_{JJ} = \gamma_{ll} = 0$  are presented under case C of Tables X, XI, and XII. Equations (12) and (13) can now be evaluated numerically, and we find that the molecular constants retain their meanings as in Eqs. (2)–(8) if

$$|q_{JJ}| \lesssim 0.001 \text{ Hz}, \quad |\gamma_{ll}| \lesssim 0.5 \text{ kHz}. \quad (14)$$

TABLE XII  
Calculated Frequencies of  $^{14}\text{N}_2^{16}\text{O}$  Rotational Transitions<sup>a</sup>

$v_1 v_2 \begin{smallmatrix}  x  \\ \tau = c, d \end{smallmatrix} v_3$	Transition $J \rightarrow J+1$	A			B			C		
		Calc. Freq. (kHz) $\nu_c$	$\nu_m - \nu_c$ (kHz)	$\nu_c$	Calc. Freq. (kHz) $\nu_c$	$\nu_m - \nu_c$ (kHz)	$\nu_c$	Calc. Freq. (kHz) $\nu_c$	$\nu_m - \nu_c$ (kHz)	$\nu_c$
$00^0_0$	14 - 15	376 777 759 ( 6 )	- 6	376 777 763 ( 5 )	- 10	376 777 763 ( 5 )	- 10	376 777 763 ( 5 )	- 10	376 777 763 ( 5 )
	15 - 16	401 885 797 ( 5 )	+ 5	401 885 800 ( 5 )	+ 2	401 885 800 ( 5 )	+ 2	401 885 800 ( 5 )	+ 2	401 885 800 ( 5 )
	16 - 17	426 991 808 ( 6 )	0	426 991 810 ( 4 )	- 2	426 991 810 ( 4 )	- 2	426 991 810 ( 4 )	- 2	426 991 810 ( 4 )
	17 - 18	452 095 666 ( 4 )	+ 4	452 095 667 ( 4 )	+ 3	452 095 667 ( 4 )	+ 3	452 095 667 ( 4 )	+ 3	452 095 667 ( 4 )
	18 - 19	477 197 244 ( 5 )	+ 3	477 197 243 ( 4 )	+ 4	477 197 243 ( 4 )	+ 4	477 197 243 ( 4 )	+ 4	477 197 243 ( 4 )
	19 - 20	502 296 417 ( 5 )	+ 6	502 296 414 ( 5 )	+ 9	502 296 414 ( 5 )	+ 9	502 296 414 ( 5 )	+ 9	502 296 414 ( 5 )
	20 - 21	527 393 058 ( 7 )	- 7	527 393 054 ( 6 )	- 3	527 393 054 ( 6 )	- 3	527 393 054 ( 6 )	- 3	527 393 054 ( 6 )
	21 - 22	552 487 041 ( 9 )	- 5	552 487 035 ( 9 )	+ 1	552 487 035 ( 8 )	+ 1	552 487 035 ( 8 )	+ 1	552 487 035 ( 8 )
$01^{1c}_0$	14 - 15	376 926 982 ( 6 )	0	376 926 979 ( 6 )	+ 3	376 926 983 ( 5 )	- 1	376 926 983 ( 5 )	- 1	376 926 983 ( 5 )
	15 - 16	402 044 835 ( 5 )	+ 1	402 044 833 ( 5 )	+ 3	402 044 834 ( 4 )	+ 2	402 044 834 ( 4 )	+ 2	402 044 834 ( 4 )
	16 - 17	427 160 635 ( 4 )	- 3	427 160 633 ( 4 )	- 1	427 160 632 ( 4 )	0	427 160 632 ( 4 )	0	427 160 632 ( 4 )
	17 - 18	452 274 253 ( 5 )	- 4	452 274 252 ( 5 )	- 3	452 274 250 ( 4 )	- 1	452 274 250 ( 4 )	- 1	452 274 250 ( 4 )
	18 - 19	477 385 561 ( 5 )	- 5	477 385 561 ( 5 )	- 5	477 385 558 ( 4 )	- 2	477 385 558 ( 4 )	- 2	477 385 558 ( 4 )
	19 - 20	502 494 432 ( 6 )	+ 1	502 494 433 ( 5 )	0	502 494 431 ( 5 )	+ 2	502 494 431 ( 5 )	+ 2	502 494 431 ( 5 )
	20 - 21	527 600 736 ( 6 )	+ 5	527 600 739 ( 6 )	+ 2	527 600 739 ( 6 )	+ 2	527 600 739 ( 6 )	+ 2	527 600 739 ( 6 )
	21 - 22	552 704 247 (10)	+ 5	552 704 351 ( 9 )	+ 1	552 704 355 ( 8 )	- 3	552 704 355 ( 8 )	- 3	552 704 355 ( 8 )
$01^{1d}_0$	14 - 15	377 638 893 ( 6 )	+ 24	377 638 890 ( 6 )	+ 27	377 638 887 ( 5 )	+ 30	377 638 887 ( 5 )	+ 30	377 638 887 ( 5 )
	15 - 16	402 804 140 ( 5 )	- 14	402 804 137 ( 5 )	- 11	402 804 136 ( 5 )	- 10	402 804 136 ( 5 )	- 10	402 804 136 ( 5 )
	16 - 17	427 967 321 ( 5 )	- 11	427 967 319 ( 4 )	- 9	427 967 320 ( 4 )	- 10	427 967 320 ( 4 )	- 10	427 967 320 ( 4 )
	17 - 18	453 128 310 ( 5 )	- 9	453 128 309 ( 5 )	- 8	453 128 311 ( 4 )	- 10	453 128 311 ( 4 )	- 10	453 128 311 ( 4 )
	18 - 19	478 286 976 ( 5 )	- 4	478 286 976 ( 5 )	- 4	478 286 979 ( 4 )	- 7	478 286 979 ( 4 )	- 7	478 286 979 ( 4 )
	19 - 20	503 443 193 ( 6 )	+ 5	503 443 195 ( 5 )	+ 3	503 443 197 ( 4 )	+ 1	503 443 197 ( 4 )	+ 1	503 443 197 ( 4 )
	20 - 21	528 596 832 ( 7 )	+ 7	528 596 835 ( 6 )	+ 4	528 596 835 ( 6 )	+ 4	528 596 835 ( 6 )	+ 4	528 596 835 ( 6 )
	21 - 22	553 747 764 (10)	0	553 747 770 ( 9 )	- 6	553 747 766 ( 8 )	- 2	553 747 766 ( 8 )	- 2	553 747 766 ( 8 )
$10^0_0$	15 - 16	400 203 022 ( 6 )	- 13	400 203 021 ( 6 )	- 12	400 203 021 ( 6 )	- 12	400 203 021 ( 6 )	- 12	400 203 021 ( 6 )
	16 - 17	425 204 102 ( 5 )	+ 10	425 204 100 ( 5 )	+ 12	425 204 101 ( 5 )	+ 11	425 204 101 ( 5 )	+ 11	425 204 101 ( 5 )
	17 - 18	450 303 074 ( 5 )	+ 11	450 303 073 ( 5 )	+ 12	450 303 072 ( 5 )	+ 13	450 303 072 ( 5 )	+ 13	450 303 072 ( 5 )
	18 - 19	475 199 813 ( 5 )	- 12	475 199 813 ( 5 )	- 12	475 199 813 ( 5 )	- 12	475 199 813 ( 5 )	- 12	475 199 813 ( 5 )
	19 - 20	500 194 199 ( 5 )	+ 7	500 194 199 ( 5 )	+ 7	500 194 199 ( 5 )	+ 7	500 194 199 ( 5 )	+ 7	500 194 199 ( 5 )
	20 - 21	525 186 106 ( 7 )	0	525 186 107 ( 7 )	- 1	525 186 107 ( 7 )	- 1	525 186 107 ( 7 )	- 1	525 186 107 ( 7 )
	21 - 22	550 175 411 (10)	- 5	550 175 416 ( 9 )	- 10	550 175 416 ( 9 )	- 10	550 175 416 ( 9 )	- 10	550 175 416 ( 9 )
$02^0_0$	14 - 15	377 566 658 ( 6 )	+ 29	377 566 658 ( 6 )	+ 29	377 566 659 ( 6 )	+ 28	377 566 659 ( 6 )	+ 28	377 566 659 ( 6 )
	15 - 16	402 723 135 ( 5 )	- 15	402 723 136 ( 5 )	- 16	402 723 136 ( 5 )	- 16	402 723 136 ( 5 )	- 16	402 723 136 ( 5 )
	16 - 17	427 876 794 ( 4 )	- 18	427 876 794 ( 4 )	- 18	427 876 794 ( 4 )	- 18	427 876 794 ( 4 )	- 18	427 876 794 ( 4 )
	17 - 18	453 027 464 ( 4 )	- 10	453 027 464 ( 4 )	- 10	453 027 464 ( 4 )	- 10	453 027 464 ( 4 )	- 10	453 027 464 ( 4 )
	18 - 19	478 174 973 ( 4 )	- 3	478 174 973 ( 4 )	- 3	478 174 973 ( 4 )	- 3	478 174 973 ( 4 )	- 3	478 174 973 ( 4 )
	19 - 20	503 319 153 ( 5 )	+ 6	503 319 153 ( 5 )	+ 6	503 319 153 ( 5 )	+ 6	503 319 153 ( 5 )	+ 6	503 319 153 ( 5 )
	20 - 21	528 459 835 ( 7 )	+ 4	528 459 835 ( 7 )	+ 5	528 459 835 ( 7 )	+ 5	528 459 835 ( 7 )	+ 5	528 459 835 ( 7 )
	21 - 22	553 596 853 ( 9 )	+ 7	553 596 853 ( 9 )	+ 7	553 596 853 ( 9 )	+ 7	553 596 853 ( 9 )	+ 7	553 596 853 ( 9 )
$02^{2d}_0$	14 - 15	377 778 541 ( 5 )	0	377 778 541 ( 5 )	0	377 778 541 ( 5 )	0	377 778 541 ( 5 )	0	377 778 541 ( 5 )
	15 - 16	402 952 970 ( 4 )	- 3	402 952 970 ( 4 )	- 3	402 952 970 ( 4 )	- 3	402 952 970 ( 4 )	- 3	402 952 970 ( 4 )
	16 - 17	428 125 310 ( 4 )	+ 8	428 125 309 ( 4 )	+ 9	428 125 309 ( 4 )	+ 9	428 125 309 ( 4 )	+ 9	428 125 309 ( 4 )
	17 - 18	453 295 428 ( 4 )	0	453 295 428 ( 4 )	0	453 295 428 ( 4 )	0	453 295 428 ( 4 )	0	453 295 428 ( 4 )
	18 - 19	478 463 196 ( 4 )	- 3	478 463 196 ( 4 )	- 3	478 463 196 ( 4 )	- 3	478 463 196 ( 4 )	- 3	478 463 196 ( 4 )
	19 - 20	503 628 483 ( 5 )	+ 4	503 628 483 ( 5 )	+ 4	503 628 483 ( 5 )	+ 4	503 628 483 ( 5 )	+ 4	503 628 483 ( 5 )
	20 - 21	528 791 159 ( 6 )	+ 3	528 791 160 ( 6 )	+ 2	528 791 159 ( 6 )	+ 3	528 791 159 ( 6 )	+ 3	528 791 159 ( 6 )
	21 - 22	553 951 095 ( 8 )	- 9	553 951 095 ( 8 )	- 9	553 951 095 ( 8 )	- 9	553 951 095 ( 8 )	- 9	553 951 095 ( 8 )

<sup>a</sup> The calculated uncertainties in parentheses are 1 SD. Columns A, B, and C are calculated from the constants given in Table X for cases A, B, and C, respectively.

Note that from variant *B* the upper limit of the constant  $|q_{JJ}|$  amounts to 0.006 Hz and the upper limit of the constant  $|\gamma_{II}|$  is 20 kHz. For the constant  $q_{JJ}$  this is rather close to the requirement of relation (14) so that we may consider its elimination to be correct. Concerning the constant  $\gamma_{II}$ , it is impossible to solve the problem of the correctness of its exclusion on the basis of available experimental data. If the constant  $\gamma_{II}$  is excluded incorrectly, the final values for the molecular constants strongly correlated with it may be more correctly given by those obtained from processing in variant *B*.<sup>3</sup>

<sup>3</sup>  $\gamma_{II}$  can be obtained using our experimental values of center frequencies of (03<sup>0</sup>) doublets. Rough estimation yields  $\gamma_{II} \sim -9$  kHz.



TABLE XII—Continued

$\nu_1 \nu_2  x  \tau_{\nu_3}$ $\tau = c, d$	Transition $J \rightarrow J+1$	A			B			C		
		Calc. Freq. (kHz)	$\nu_m - \nu_c$	(kHz)	Calc. Freq. (kHz)	$\nu_m - \nu_c$	(kHz)	Calc. Freq. (kHz)	$\nu_m - \nu_c$	(kHz)
		$\nu_c$	( $\Delta\nu_c$ )		$\nu_c$	( $\Delta\nu_c$ )		$\nu_c$	( $\Delta\nu_c$ )	
02 <sup>2</sup> c <sub>0</sub>	14 - 15	377 802 552 (5)	- 17		377 802 553 (5)	- 18		377 802 553 (4)	- 18	
	15 - 16	402 982 082 (4)	+ 6		402 982 084 (4)	+ 4		402 982 083 (4)	+ 5	
	16 - 17	428 160 186 (4)	+ 9		428 160 187 (4)	+ 8		428 160 187 (4)	+ 8	
	17 - 18	453 336 770 (4)	+ 5		453 336 770 (4)	+ 5		453 336 770 (4)	+ 5	
	18 - 19	478 511 739 (4)	- 2		478 511 740 (4)	- 3		478 511 740 (4)	- 3	
	19 - 20	503 685 001 (5)	+ 4		503 685 000 (5)	+ 5		503 685 001 (5)	+ 4	
	20 - 21	528 856 456 (6)	+ 6		528 856 455 (6)	+ 7		528 856 455 (6)	+ 7	
	21 - 22	554 026 009 (8)	- 11		554 026 007 (8)	- 9		554 026 007 (8)	- 9	
11 <sup>1</sup> d <sub>0</sub>	16 - 17	425 416 318 (21)	+ 13		425 416 335 (15)	- 4		425 416 334 (15)	- 3	
	17 - 18	450 427 620 (18)	+ 22		450 427 631 (15)	+ 11		450 427 629 (15)	+ 13	
	18 - 19	475 436 661 (16)	- 38		475 436 665 (15)	- 42		475 436 663 (15)	- 40	
	19 - 20	500 443 317 (15)	+ 22		500 443 316 (15)	+ 23		500 443 314 (15)	+ 25	
	20 - 21	525 447 465 (18)	+ 10		525 447 455 (16)	+ 20		525 447 456 (16)	+ 19	
	21 - 22	550 448 976 (25)	- 26		550 448 960 (20)	- 10		550 448 965 (19)	- 15	
11 <sup>1</sup> c <sub>0</sub>	16 - 17	426 343 982 (23)	- 27		426 343 999 (20)	- 44		426 343 999 (14)	- 44	
	17 - 18	451 410 056 (19)	0		451 410 067 (17)	- 12		451 410 068 (14)	- 12	
	18 - 19	476 473 907 (16)	- 21		476 473 912 (15)	- 26		476 473 915 (14)	- 29	
	19 - 20	501 535 415 (15)	+ 49		501 535 414 (15)	+ 50		501 535 416 (15)	+ 48	
	20 - 21	526 594 458 (19)	+ 10		526 594 449 (18)	+ 19		526 594 448 (16)	+ 20	
	21 - 22	551 650 912 (26)	- 15		551 650 896 (24)	+ 1		551 650 891 (18)	+ 6	
03 <sup>1</sup> c <sub>0</sub>	14 - 15	377 279 303 (20)	0		377 279 303 (20)	0		377 279 309 (18)	- 6	
	15 - 16	402 418 733 (17)	+ 14		402 418 733 (17)	+ 14		402 418 734 (16)	+ 13	
	16 - 17	427 555 747 (15)	+ 8		427 555 747 (15)	+ 8		427 555 745 (15)	+ 10	
	17 - 18	452 690 200 (14)	- 8		452 690 200 (14)	- 8		452 690 195 (14)	- 3	
	18 - 19	477 821 941 (14)	+ 4		477 821 941 (14)	+ 4		477 821 935 (13)	+ 10	
	19 - 20	502 950 825 (15)	+ 2		502 950 825 (15)	+ 2		502 950 821 (14)	+ 6	
	20 - 21	528 076 705 (18)	0		528 076 706 (18)	0		528 076 705 (18)	+ 1	
	21 - 22	553 199 435 (26)	- 16		553 199 435 (25)	- 16		553 199 444 (23)	- 25	
03 <sup>3</sup> c <sub>0</sub>	14 - 15	378 273 332 (59)			378 273 419 (25)			378 273 420 (24)		
	16 - 17	428 688 513 (75)			428 688 628 (30)			428 688 629 (30)		
	17 - 18	453 893 157 (85)			453 893 288 (34)			453 893 289 (33)		
	18 - 19	479 095 676 (96)			479 095 824 (40)			479 095 825 (40)		
	19 - 20	504 295 947 (109)			504 296 115 (44)			504 296 115 (44)		
	20 - 21	529 493 852 (122)			529 494 038 (50)			529 494 038 (49)		
	21 - 22	554 689 264 (136)			554 689 472 (57)			554 689 473 (55)		
03 <sup>3</sup> d <sub>0</sub>	14 - 15	378 273 580 (61)			378 273 672 (25)			378 273 672 (25)		
	16 - 17	428 688 976 (81)			428 689 100 (32)			428 689 101 (32)		
	17 - 18	453 893 773 (93)			453 893 915 (36)			453 893 916 (36)		
	18 - 19	479 096 482 (106)			479 096 645 (42)			479 096 646 (41)		
	19 - 20	504 296 987 (122)			504 297 174 (48)			504 297 175 (47)		
	20 - 21	529 495 177 (138)			529 495 389 (55)			529 495 389 (53)		
	21 - 22	554 690 933 (157)			554 691 173 (64)			554 691 173 (61)		
03 <sup>1</sup> d <sub>0</sub>	14 - 15	378 620 819 (20)	- 88		378 620 823 (18)	- 92		378 620 817 (16)	- 86	
	15 - 16	403 849 247 (18)	+ 16		403 849 251 (16)	+ 12		403 849 249 (15)	+ 14	
	16 - 17	429 075 166 (16)	+ 50		429 075 169 (15)	+ 47		429 075 171 (14)	+ 45	
	17 - 18	454 298 420 (14)	+ 9		454 298 423 (14)	+ 6		454 298 427 (13)	+ 2	
	18 - 19	479 518 853 (14)	- 6		479 518 853 (14)	- 6		479 518 858 (13)	- 11	
	19 - 20	504 736 306 (15)	+ 20		504 736 305 (15)	+ 21		504 736 309 (14)	+ 17	
	20 - 21	529 950 625 (19)	+ 13		529 950 621 (17)	+ 17		529 950 621 (17)	+ 17	
	21 - 22	555 161 651 (26)	- 24		555 161 644 (23)	- 17		555 161 636 (21)	- 10	

2. Let us consider the results of processing all data for each of the isotopic species <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O, and <sup>14</sup>N<sub>2</sub><sup>18</sup>O. There is available nearly the same set of rotational transition frequencies in the vibrational states (00<sup>0</sup>), (01<sup>1</sup>0), and (01<sup>1</sup>0) for each of these isotopic species and the data reduction procedure is identical for all of them. For the data considered, the conditions

$$\nu_1 = 0, \quad \nu_2^2 = \nu_2, \quad \nu_3 = 0, \quad |l|^2 = |l|, \quad \nu_2 = |l| \quad (15)$$

are satisfied. In analogy to the selection of constants in the case of <sup>14</sup>N<sub>2</sub><sup>16</sup>O, one finds the following independent molecular constants: rotational and centrifugal stretching constants in the ground vibrational state,  $B_0$ ,  $D_0$ , and  $H_0$ ; the constants of nonresonant

TABLE XIII  
Molecular Constants of  $^{15}\text{N}^{14}\text{N}^{16}\text{O}^a$

		A	B
$B_0$	MHz	12 137.3104 (20)	12 137.3104 (20)
$\alpha_2^{**}$	MHz	- 16.5321 (14)	- 16.5321 (14)
$B_{11}$	kHz	4.8898 (54)	4.8898 (54)
$\alpha_2$	kHz	- 0.0748 (16)	- 0.0748 (16)
$H_0$	Hz	- 0.0112 (45)	- 0.0112 (45)
$q_{(010)}$	MHz	11.1425 (73)	11.1457 (13)
$q_J$	kHz	- 0.006 (18)	- 0.0140 (15)
$q_{JJ}$	Hz	- 0.006 (14)	0

<sup>a</sup> Theoretical description was performed in accordance with Eqs. (2)–(8) for the following cases: (A) Experimental frequencies of rotational spectra listed in Table II were used. (B) In addition to case “A” the condition  $q_{JJ} = 0$  was used.

rotation–vibration interaction,  $\alpha_2^{**}$  and  $\beta_2$  ( $\alpha_2^{**} = \alpha_2^* - \gamma_{11} = \alpha_2 - \gamma_{12} - 2\gamma_{22} - \gamma_{23} - \gamma_{11}$ ); the constants involved in the matrix elements of  $l$ -type resonance,  $q_{(010)}$ ,  $q_J$ , and  $q_{JJ}$ . The maximum number of the molecular constants to be determined for these isotopic species in processing the rotational spectrum is equal to 8. The molecular constants obtained in this full variant, the matrix of their correlation coefficients, as well as the calculated spectral line frequencies are given in columns A of Tables XIII, XIV, and XV (for the isotopic species  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ ; Tables XVI, XVII, and XVIII (for the

TABLE XIV  
Matrix Correlation Coefficients for  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  Molecular Constants

Case “A”							
	$B_0$	$\alpha_2^{**}$	$B_{11}$	$\alpha_2$	$H_0$	$q_{(010)}$	$q_J$
$B_0$	1						
$\alpha_2^{**}$	- 0.12	1					
$B_{11}$	+ 0.99	- 0.17	1				
$\alpha_2$	- 0.11	+ 0.98	- 0.16	1			
$H_0$	+ 0.98	- 0.20	+ 0.99	- 0.19	1		
$q_{(010)}$	- 0.00	+ 0.00	- 0.00	+ 0.00	- 0.00	1	
$q_J$	+ 0.00	- 0.00	+ 0.00	- 0.00	- 0.00	- 0.00	1
$q_{JJ}$	- 0.00	+ 0.00	- 0.00	- 0.00	- 0.00	+ 0.98	- 0.00

Case “B”							
	$B_0$	$\alpha_2^{**}$	$B_{11}$	$\alpha_2$	$H_0$	$q_{(010)}$	$q_J$
$B_0$	1						
$\alpha_2^{**}$	- 0.12	1					
$B_{11}$	+ 0.99	- 0.17	1				
$\alpha_2$	- 0.11	+ 0.98	- 0.16	1			
$H_0$	+ 0.98	- 0.20	+ 0.99	- 0.19	1		
$q_{(010)}$	- 0.00	+ 0.00	- 0.00	+ 0.00	- 0.00	1	
$q_J$	+ 0.00	- 0.00	- 0.00	- 0.00	- 0.00	- 0.98	1

TABLE XV  
Frequencies of <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O Rotational Transitions<sup>a</sup>

$v_1 v_2 \begin{smallmatrix}  x  \\ \tau \end{smallmatrix} v_3$ $\tau = c, d$	Transition $J \rightarrow J + 1$	A		B	
		Calc. Freq. (kHz)		Calc. Freq. (kHz)	
		$\nu_c$	$(\nu_c)$	$\nu_c$	$(\nu_c)$
00 <sup>0</sup> <sub>0</sub>	15 - 16	388 313 748 ( 7)	- 12	388 313 748 ( 7)	- 12
	16 - 17	412 572 365 ( 5)	+ 20	412 572 365 ( 5)	+ 20
	17 - 18	436 828 979 ( 5)	- 1	436 828 979 ( 5)	- 1
	18 - 19	461 083 473 ( 5)	- 1	461 083 473 ( 5)	- 1
	19 - 20	485 335 729 ( 6)	0	485 335 729 ( 6)	0
	20 - 21	509 585 627 ( 6)	- 7	509 585 627 ( 6)	- 7
	21 - 22	533 833 047 ( 7)	- 1	533 833 047 ( 7)	- 1
	22 - 23	558 077 872 (11)	+ 5	558 077 872 (11)	+ 5
01 <sup>1c</sup> <sub>0</sub>	16 - 17	412 754 651 (27)	+ 13	412 754 645 (23)	+ 19
	17 - 18	437 021 830 (19)	- 55	437 021 829 (19)	- 54
	18 - 19	461 286 864 (17)	+ 63	461 286 866 (16)	+ 61
	19 - 20	485 549 632 (18)	+ 4	485 549 637 (14)	- 1
	20 - 21	509 810 015 (18)	- 32	509 810 020 (15)	- 37
	21 - 22	534 067 895 (19)	- 1	534 067 896 (19)	- 2
	22 - 23	558 323 150 (30)	+ 8	558 323 144 (27)	+ 14
01 <sup>1d</sup> <sub>0</sub>	16 - 17	413 511 996 (27)	+ 7	413 512 002 (23)	+ 1
	17 - 18	437 823 665 (19)	- 11	437 823 666 (19)	- 12
	18 - 19	462 133 174 (17)	- 2	462 133 171 (16)	+ 1
	19 - 20	486 440 402 (18)	+ 9	486 440 397 (14)	+ 14
	20 - 21	510 745 227 (18)	- 2	510 745 222 (15)	+ 3
	21 - 22	535 047 527 (19)	- 5	535 047 526 (19)	- 4
	22 - 23	559 347 181 (30)	+ 3	559 347 187 (27)	- 3

<sup>a</sup> The frequencies were calculated in accordance with Eqs. (2)–(8) for the following cases: (A) By the use of experimental frequencies ( $\nu_m$ ) listed in Table II. (B) In addition to case “A” the condition  $q_{JJ} = 0$  was used.

isotopic species <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O); and Tables XIX, XX, and XXI (for the isotopic species <sup>14</sup>N<sub>2</sub><sup>18</sup>O). It is easy to see that in describing the available experimental data one does not succeed in distinguishing the contribution of the strongly correlated constants  $q_J$  and  $q_{JJ}$ . Therefore we consider the results of the variant with the constant  $q_{JJ}$  omitted, given in columns B of the above-listed tables. The accuracy of definition of the molecular constants  $q_{(010)}$  and  $q_J$ , which are strongly correlated with  $q_{JJ}$ , is significantly higher than in variant A. The requirement given by Eq. (12) for the two former constants to

TABLE XVI  
Molecular Constants of <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O<sup>a</sup>

		A		B	
$B_0$	MHz	12 560.7309 (19)		12 560.7310 (19)	
$\alpha_2$	MHz	- 15.9330 (14)		- 15.9332 (14)	
$D_0$	kHz	5.2677 (57)		5.2680 (57)	
$\tau_2$	kHz	- 0.0800 (18)		- 0.0802 (18)	
$H_0$	Hz	- 0.0086 (53)		- 0.0083 (53)	
$q_{(010)}$	MHz	12.1431 (59)		12.1398 (13)	
$q_J$	kHz	- 0.023 (16)		- 0.0142 (17)	
$q_{JJ}$	Hz	- 0.008 (15)		0	

<sup>a</sup> Theoretical description was performed in accordance with Eqs. (2)–(8) for the following cases: (A) Experimental frequencies of rotational spectra listed in Table III were used. (B) In addition to case “A” the condition  $q_{JJ} = 0$  was used.

TABLE XVII  
Matrix Correlation Coefficients for  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  Molecular Constants

Case "A"								
	$B_0$	$\beta_2$	$D_0$	$\beta_2$	$H_0$	$q_{(010)}$	$q_J$	$q_{JJ}$
$B_0$	1							
$\beta_2$	-0.08	1						
$D_0$	+0.99	-0.12	1					
$\beta_2$	-0.07	+0.98	-0.12	1				
$H_0$	+0.97	-0.16	+0.99	-0.15	1			
$q_{(010)}$	-0.11	+0.28	-0.11	+0.26	-0.11	1		
$q_J$	+0.10	-0.25	+0.10	-0.23	+0.11	-0.99	1	
$q_{JJ}$	-0.10	+0.22	-0.10	+0.21	-0.10	+0.98	-0.99	1

  

Case "B"								
	$B_0$	$\beta_2$	$D_0$	$\beta_2$	$H_0$	$q_{(010)}$	$q_J$	
$B_0$	1							
$\beta_2$	-0.06	1						
$D_0$	+0.99	-0.10	1					
$\beta_2$	-0.05	+0.98	-0.10	1				
$H_0$	+0.97	-0.14	+0.99	-0.14	1			
$q_{(010)}$	-0.08	+0.29	-0.08	+0.26	-0.08	1		
$q_J$	+0.08	-0.27	+0.08	-0.24	+0.08	-0.98	1	

retain their physical meaning leads to the condition

$$|q_{JJ}| \lesssim 0.005 \text{ Hz.} \quad (16)$$

Since the upper limit  $|q_{JJ}|$  is of the order of 0.02 Hz from the fit to the full set of constants, the correctness of excluding this constant is not quite obvious. It should be noted that it is also difficult to determine the upper limit of  $|q_{JJ}|$  using the main isotopic species data (see part B of Table X). The expressions for the molecular constants involved in the corrections on the rovibrational second- or higher-order energy terms are expressed through the structural and force constants of the molecule in the form of a linear combination of some functions of these parameters. The functions are of the same order of magnitude and have, as a rule, different signs (15). As a result, isotopic substitution may even lead to a change of the sign of the molecular constant, as observed, for example, in the case of the molecule  $\text{N}_2\text{O}$  for the fourth-order centrifugal stretching constant  $H_0$ :

$$\begin{aligned}
 H_0 &= +0.0059(22) \text{ Hz, } ^{14}\text{N}_2^{16}\text{O}; \\
 &= -0.004(20) \text{ Hz, } ^{14}\text{N}_2^{17}\text{O}; \\
 &= -0.0083(53) \text{ Hz, } ^{14}\text{N}^{15}\text{N}^{16}\text{O}; \\
 &= -0.0112(45) \text{ Hz, } ^{15}\text{N}^{14}\text{N}^{16}\text{O}; \\
 &= -0.0114(47) \text{ Hz, } ^{14}\text{N}_2^{18}\text{O}.
 \end{aligned}$$

TABLE XVIII  
Frequencies of <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O Rotational Transitions<sup>a</sup>

$v_1 v_2 \begin{smallmatrix}   \\ \tau \end{smallmatrix} \begin{smallmatrix}   \\ \tau \end{smallmatrix} v_3 \\ \tau = c, d$	Transition J → J + 1	A		B	
		Calc. Freq. (kHz)		Calc. Freq. (kHz)	
		$\nu_c$	( $\nu_c$ )	$\nu_c$	( $\nu_c$ )
00 <sup>0</sup> <sub>0</sub>	14 - 15	376 750 773	( 7)	376 750 773	( 7)
	15 - 16	401 857 028	( 5)	401 857 028	( 5)
	16 - 17	426 961 256	( 5)	426 961 256	( 5)
	17 - 18	452 063 329	( 5)	452 063 329	( 5)
	18 - 19	477 163 121	( 6)	477 163 121	( 6)
	19 - 20	502 260 504	( 6)	502 260 504	( 6)
	20 - 21	527 355 350	( 7)	527 355 350	( 7)
	21 - 22	552 447 532	(11)	552 447 533	(11)
01 <sup>1c</sup> <sub>0</sub>	15 - 16	401 977 671	(31)	401 977 678	(26)
	17 - 18	452 198 740	(19)	452 198 738	(19)
	18 - 19	477 305 872	(18)	477 305 867	(16)
	19 - 20	502 410 562	(18)	502 410 557	(16)
	20 - 21	527 512 681	(19)	527 512 679	(19)
	21 - 22	552 612 097	(30)	552 612 103	(27)
01 <sup>1d</sup> <sub>0</sub>	14 - 15	377 592 020	(26)	377 592 011	(21)
	15 - 16	402 754 164	(19)	402 754 161	(18)
	16 - 17	427 914 246	(16)	427 914 248	(16)
	17 - 18	453 072 137	(17)	453 072 142	(14)
	18 - 19	478 227 707	(18)	478 227 713	(14)
	19 - 20	503 380 828	(18)	503 380 833	(15)
	20 - 21	528 531 370	(19)	528 531 371	(19)
	21 - 22	553 679 205	(30)	553 679 196	(26)

<sup>a</sup> The frequencies, were calculated in accordance with Eqs. (2)–(8) for the following cases: (A) By the use of experimental frequencies ( $\nu_m$ ) listed in Table III. (B) In addition to case “A” the condition  $q_{JJ} = 0$  was used.

3. For the isotopic species <sup>14</sup>N<sub>2</sub><sup>17</sup>O we have the experimental data on the rotational spectrum only for the ground vibrational state (00<sup>0</sup>). Therefore, the variant yielding the most complete set of constants,  $B_0$ ,  $D_0$ ,  $H_0$ , has already been carried out (see Tables V and VI). Here we analyze the variant with the poorly defined constant  $H_0$  excluded. The results of this calculation are given in Table XXII. It is easy to see that the accuracy of the molecular constants  $B_0$  and  $D_0$ , which are strongly correlated

TABLE XIX  
Molecular Constants of <sup>14</sup>N<sub>2</sub><sup>18</sup>O<sup>a</sup>

		A	B
$\nu_0$	MHz	11 859.1102 (21)	11 859.1100 (21)
$\alpha_2^x$	MHz	- 16.1028 (17)	- 16.1024 (17)
$\nu_0$	kHz	4.7285 (55)	4.7280 (55)
$\nu_2$	kHz	- 0.0702 (19)	- 0.0698 (19)
$H_0$	Hz	- 0.0109 (47)	- 0.0114 (47)
$q(010)$	MHz	10.6816 (89)	10.6723 (15)
$q_J$	kHz	- 0.037 (22)	- 0.0145 (17)
$q_{JJ}$	Hz	0.018 (17)	0

<sup>a</sup> Theoretical description was performed in accordance with Eqs. (2)–(8) for the following cases: (A) Experimental frequencies of rotational spectra listed in Table IV were used. (B) In addition to case “A” the condition  $q_{JJ} = 0$  was used.

TABLE XX  
Matrix Correlation Coefficients for  $^{14}\text{N}_2^{18}\text{O}$  Molecular Constants

Case "A"

	$B_0$	$\frac{C}{2}$	$D_0$	$\frac{E}{2}$	$H_0$	$q_{(010)}$	$q_J$	$q_{JJ}$
$B_0$	1							
$\frac{C}{2}$	- 0.19	1						
$D_0$	+ 0.99	- 0.23	1					
$\frac{E}{2}$	- 0.18	+ 0.99	- 0.22	1				
$H_0$	+ 0.98	- 0.26	+ 0.99	- 0.25	1			
$q_{(010)}$	+ 0.09	- 0.23	+ 0.09	- 0.21	+ 0.10	1		
$q_J$	- 0.09	+ 0.22	- 0.09	+ 0.21	- 0.09	- 1.00	1	
$q_{JJ}$	+ 0.08	- 0.21	+ 0.09	- 0.20	+ 0.09	+ 0.99	- 1.00	1

Case "B"

	$B_0$	$\frac{C}{2}$	$D_0$	$\frac{E}{2}$	$H_0$	$q_{(010)}$	$q_J$
$B_0$	1						
$\frac{C}{2}$	- 0.18	1					
$D_0$	+ 0.99	- 0.21	1				
$\frac{E}{2}$	- 0.17	+ 0.99	- 0.21	1			
$H_0$	+ 0.98	- 0.24	+ 0.99	- 0.24	1		
$q_{(010)}$	+ 0.06	- 0.09	+ 0.06	- 0.09	+ 0.06	1	
$q_J$	- 0.05	+ 0.09	- 0.06	+ 0.09	- 0.06	- 0.99	1

with  $H_0$ , are significantly improved. For the remaining molecular constants to keep their physical meaning, the following condition for the constant neglected must be fulfilled.

$$|H_0| \lesssim 0.01 \text{ Hz.} \quad (17)$$

The upper limit of  $H_0$  is of the order of 0.02 Hz, which is rather close to the requirement of relation (17).

## CONCLUSION

The investigation of the rotational spectrum of the molecule  $\text{N}_2\text{O}$  is a pioneer effort in systematic research in the submillimeter wave region of the molecular spectrum by means of a RAD spectrometer. The results obtained are uniquely extensive and exhibit the high efficiency of these methods.

The rotational spectral lines of  $\text{N}_2\text{O}$  in the submillimeter wave region reach their maximum intensity at  $J \rightarrow J + 1 = 27 \rightarrow 28$ ,  $\nu_{\text{opt}} \cong 700 \text{ GHz}$ . It is clearly seen that in this region they are strongly affected by molecular nonrigidity effects. This fact, combined with the high sensitivity and large operating bandwidth of the spectrometer, results in data rich in information about the molecular spectrum. In particular, using microwave methods we could observe for the first time rotational lines in the excited vibrational states  $(11^1c0)$ ,  $(11^1d0)$ ,  $(03^3c,d0)$ ,  $(03^1c0)$ ,  $(03^1d0)$ ,  $(E_{\text{vib}} \cong 1800 \text{ cm}^{-1})$ ; in the excited vibrational states  $(01^1c0)$ ,  $(01^1d0)$  of the isotopic species  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ,  $^{14}\text{N}_2^{18}\text{O}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ , and in the ground vibrational state of the isotopic species  $^{14}\text{N}_2^{17}\text{O}$ . The great number of the spectral lines observed and the high accuracy of frequency measurement

TABLE XXI  
Frequencies of <sup>14</sup>N<sub>2</sub> <sup>18</sup>O Rotational Transitions<sup>a</sup>

$\nu_1 \nu_2 \begin{smallmatrix}  k  \\ \tau \end{smallmatrix} \nu_3$ $\tau = c, d$	Transition $J \rightarrow J + 1$	A		B	
		Calc. Freq. (kHz) $\nu_c$	$(\nu_c)$	Calc. Freq. (kHz) $\nu_c$	$(\nu_c)$
00 <sup>0</sup> <sub>0</sub>	15 - 16	379 413 985 ( 7)	- 17	379 413 984 ( 7)	- 16
	16 - 17	403 116 728 ( 5)	+ 19	403 116 728 ( 5)	+ 19
	17 - 18	426 817 535 ( 5)	+ 10	426 817 536 ( 5)	+ 9
	18 - 19	450 516 293 ( 5)	+ 2	450 516 293 ( 5)	+ 2
	19 - 20	474 212 884 ( 6)	- 14	474 212 885 ( 6)	- 15
	20 - 21	497 907 196 ( 6)	- 1	497 907 196 ( 6)	- 1
	21 - 22	521 599 112 ( 7)	- 6	521 599 112 ( 7)	- 6
	22 - 23	545 288 518 (11)	+ 8	545 288 518 (11)	+ 8
01 <sup>1</sup> <sub>c0</sub>	16 - 17	403 300 575 (32)	+ 9	403 300 593 (27)	- 9
	18 - 19	450 721 493 (20)	+ 7	450 721 487 (19)	+ 13
	19 - 20	474 428 719 (20)	- 27	474 428 707 (16)	- 15
	20 - 21	498 133 631 (19)	+ 4	498 133 619 (15)	+ 16
	21 - 22	521 836 112 (19)	+ 2	521 836 108 (19)	+ 6
	22 - 23	545 536 041 (31)	+ 5	545 536 057 (27)	- 11
01 <sup>1</sup> <sub>d0</sub>	17 - 18	427 779 818 (27)	+ 13	427 779 805 (24)	+ 26
	18 - 19	451 531 785 (20)	+ 21	451 531 785 (20)	+ 21
	19 - 20	475 281 552 (18)	- 69	475 281 561 (16)	- 78
	20 - 21	499 029 005 (18)	+ 44	499 029 016 (15)	+ 33
	21 - 22	522 774 028 (20)	- 17	522 774 033 (19)	- 22
	22 - 23	546 516 507 (30)	+ 9	546 516 495 (28)	+ 21

<sup>a</sup> The frequencies were calculated in accordance with Eqs. (2)–(8) for the following cases: (A) By the use of experimental frequencies ( $\nu_m$ ) listed in Table IV. (B) In addition to case "A" the condition  $q_{JJ} = 0$  was used.

( $\sim 10^{-8}$ ) now made it possible to define the most precise values of some fundamental molecular constants by processing simultaneously all experimental data within each isotopic species taking account of the resonance effects. By considering correlation properties of the solutions of the inverse problem it was possible to decrease correctly the number of molecular constants to be determined without changing their physical meaning.

The use of additional data from infrared measurements in some variants of processing improved the determination of a number of molecular constants, in particular, those describing the Fermi resonance, and did not worsen the fit of the microwave data. Because of this one may hope for a good joint analysis of the full set of ir and mw experimental data on the rovibrational spectrum of the molecule N<sub>2</sub>O.

TABLE XXII  
Molecular Constants, Correlation Coefficient, and Calculated Frequencies of <sup>14</sup>N<sub>2</sub> <sup>17</sup>O Rotational Transitions in the (000) Vibrational State, According to Eq. (1)<sup>a</sup>

Transition $J \rightarrow J + 1$	Calc. Freq. (kHz) $\nu_c$	$(\Delta\nu_c)$	$\nu_m - \nu_c$ (kHz)
16 - 17	414 420 409 (22)		- 13
17 - 18	438 785 502 (18)		+ 6
18 - 19	463 148 438 (16)		+ 10
19 - 20	487 509 099 (14)		+ 8
20 - 21	511 867 363 (15)		- 7
21 - 22	536 223 112 (18)		- 8
22 - 23	560 576 225 (26)		+ 3

<sup>a</sup> The experimental frequencies given in Table V were used to obtain the constants.  $H_\tau$  was constrained to zero. The uncertainties given in parentheses after the constants are standard errors, and those after the calculated frequencies are 1 SD.

The most immediate application of the molecular constants obtained for different isotopic species of the molecule  $\text{N}_2\text{O}$  may be a significant refinement of structural and force field parameters of the molecule.

#### APPENDIX

On the assumption of a Lorentzian lineshape for a line "1" whose apparent maximum is shifted by the nearness of line "2," one may obtain in the first approximation

$$\Delta\nu_{\text{sh}} = \nu_1 - \nu_1^0 = (\gamma_2/\gamma_1)\Delta\nu[(\nu_2^0 - \nu_1^0)]^3. \quad (1.1)$$

Here  $\Delta\nu_{\text{sh}} = \nu_1 - \nu_1^0$  is the shift of the center of line "1" from the unperturbed position of  $\nu_1^0$  toward line "2";  $\nu_2^0$  is the unperturbed position of the center of line "2";  $\gamma_1$  and  $\gamma_2$  are the absorption coefficients of lines "1" and "2," respectively;  $\Delta\nu$  is the collisional line half-width. It is not difficult to see that the shift depends strongly both on pressure and on the spacing between lines. Estimates show that this effect may be neglected in the present work for all observed rotational transitions except for the transitions of the isotopic species  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  at an operating pressure of 0.5 Torr. The rotational transitions of this isotopic species in the ground vibrational state were measured both at that pressure and at 0.1 Torr, for which the effect on these lines is small. To correct the transition frequencies in the vibrational states  $(01^10)$  and  $(01^40)$ , which were measured only at 0.5 Torr, the effective parameter  $\Delta\nu_{\text{sh}}$  used in formula (1.1) was determined from the frequency shift of the ground vibrational state lines. It is evident that the values of absolute pressure measurement errors are not important in such a method.

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