

# The application of a vacuum ultraviolet Fourier transform spectrometer and synchrotron radiation source to measurements of: IV. The $\beta(6,0)$ and $\gamma(3,0)$ bands of NO

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The  $\beta(6,0)$  ( $B^2\Pi_r-X^2\Pi_r$ ) and  $\gamma(3,0)$  ( $A^2\Sigma^+-X^2\Pi_r$ ) bands of NO have been recorded using a vacuum ultraviolet Fourier transform spectrometer with synchrotron radiation as light source. The analysis of the  $\beta(6,0)$  and  $\gamma(3,0)$  bands of NO provides accurate rotational line positions and term values. Molecular constants of the  $v=6$  level of the  $B^2\Pi_r$  and  $v=3$  level of the  $A^2\Sigma^+$  have been determined. Accurate rotational line strengths have also been obtained. The band oscillator strength of the  $\beta(6,0)$  and  $\gamma(3,0)$  bands are determined to be  $0.48 \times 10^{-4}$  and  $2.69 \times 10^{-4}$ , respectively. © 2002 American Institute of Physics. [DOI: 10.1063/1.1421064]

## I. INTRODUCTION

In the wavelength region 175–205 nm the penetration of solar radiation into the atmosphere is controlled by the absorption cross sections of the Schumann–Runge bands of  $O_2$ . Part of the radiation transmitted is available to photopredissociate NO, which has a number of strong bands with very narrow lines in the region 183–195 nm. With recent advancement of new spectroscopic techniques, we thought it would be beneficial to record and analyze these NO systems with a resolution that is comparable to the Doppler width to obtain accurate line positions and, more importantly, the band oscillator strengths of these bands. Discussions on the necessity for high resolution measurements of NO have been presented in previous papers of the series on NO bands.<sup>1–3</sup> In these papers we describe how we combined high-resolution vacuum ultraviolet (VUV) Fourier transform (FT) spectrometry with synchrotron radiation by taking the Imperial College (IC) VUV FT spectrometer to the synchrotron radiation source at Photon Factory, KEK, Japan, where a suitable zero dispersion two-grating predisperser is available on beam line 12-B. (The predisperser is necessary to limit the bandwidth to a few nm in order to achieve acceptable signal-to-noise ratios, S/N.) We have used this combination of facilities to make ultra high resolution cross-section measurements of NO in the wavelength region 195–160 nm. The present paper in this series presents the spectroscopic analysis and the

line and band oscillator strengths of the  $\beta(6,0)$  ( $B^2\Pi_r-X^2\Pi_r$ ) and  $\gamma(3,0)$  ( $A^2\Sigma^+-X^2\Pi_r$ ) bands of NO.

An extensive review of the earlier experimental work on the electronic spectrum of NO molecules is given by Miescher and Huber.<sup>4</sup> The absorption spectra of NO were photographed in the VUV region for the first time by Leifson.<sup>5</sup> He noticed the three groups of band systems, now known to be the  $\gamma$ ,  $\beta$ , and  $\epsilon$  bands. Herzberg and Mundie<sup>6</sup> observed anomalous intensity distribution in the NO bands and assumed that the  $\epsilon$  bands are a continuation of the  $\gamma$  bands. Tanaka<sup>7</sup> investigated the absorption bands of NO, and confirmed anomalous intensity in the  $\gamma$  bands. He assigned the  $\gamma$  bands up to  $v'=7$  by following the comments of Herzberg and Mundie. The existence of both the  $\gamma$  and  $\epsilon$  bands was confirmed by observation of the  $\gamma(4,0)$  band in the  $\epsilon(0,0)$  band by Herzberg *et al.*<sup>8</sup> However, the  $\gamma(3,0)$  band has never been analyzed rotationally in absorption. The molecular constants of the  $v=3$  level of the  $A^2\Sigma^+$  state have been available from observation in emission.<sup>9–11</sup> Recently Danielak *et al.*<sup>12</sup> reinvestigated in emission the  $\gamma$  bands of NO including the (3,0) band with a high resolution grating instrument. The  $\beta(6,0)$  band of NO was studied extensively by Miescher and co-workers.<sup>8,13</sup> They observed the (5,0) to (19,0) bands of the  $\beta$  system in absorption by using a medium resolution grating instrument, and presented the rotational constant for the  $B(6)$  level.

The cross section measurements of the  $B(6)-X(0)$  and  $A(3)-X(0)$  bands by Bethke<sup>14</sup> were performed at low resolution, 0.04 nm, in the presence of Ar. The rotational lines were pressure broadened to well beyond the instrumental

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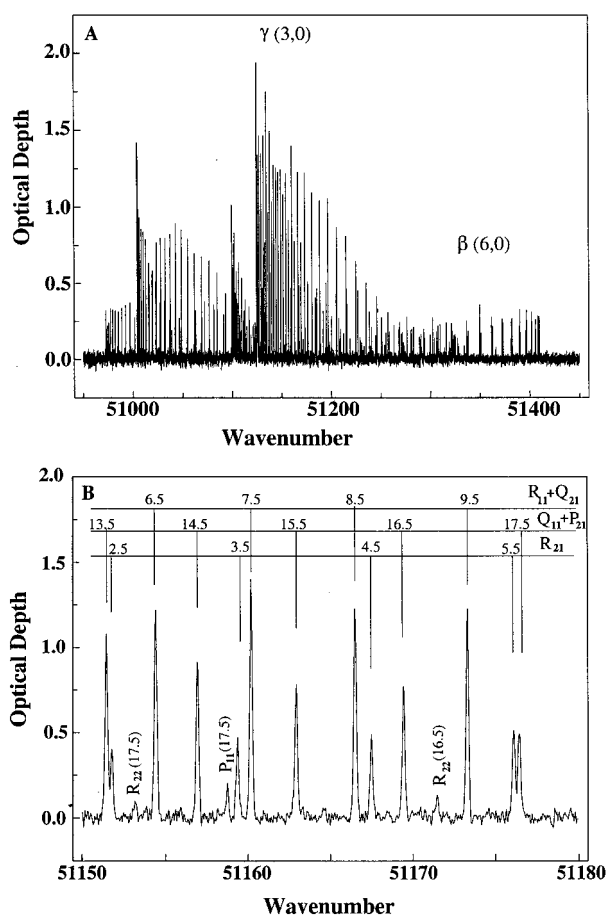


FIG. 1. The  $\beta(6,0)$  and  $\gamma(3,0)$  bands at 0.300 Torr of NO with 7.54 cm path length is shown in Fig. 1(A). An expanded portion of the spectrum with the transition assignments is displayed in Fig. 1(B).

width, enabling the true cross sections to be measured. Farmer *et al.*<sup>15</sup> used the “Hook” technique to measure the band oscillator strengths of the  $\gamma$  bands of NO including the (3,0) band. Cieslik<sup>16</sup> made low resolution measurements of NO at low pressure and used the equivalent width and curve of growth method to obtain the band oscillator strength of the  $A(3)-X(0)$  band. Chan *et al.*<sup>17</sup> used the high resolution dipole ( $e, e$ ) technique, which is not sensitive to the instrumental resolution. Laux and Kruger<sup>18</sup> calculated *ab initio* the band oscillator strengths for the  $\gamma$  band. Luque and Crosley<sup>19</sup> also obtained the band oscillator strengths from the lifetime measurements after two photon excitation.

In this paper, we report the analysis of the  $\beta(6,0)$  and the  $\gamma(3,0)$  bands of NO near 198 nm by using the VUV FT spectrometer with synchrotron radiation for the background source. Accurate line positions and line strengths of the rotational lines have been retrieved from our FT spectra. The rotational term values of the  $B^2\Pi_r$  ( $v=6$ ) and  $A^2\Sigma^+$  ( $v=3$ ) levels have been evaluated and then fed to a least squares fitting program to obtain accurate molecular constants of these levels. Since the resolution of the present experiment is comparable to the Doppler widths, the determination of the band oscillator strengths of these bands has been performed using line by line measurements.

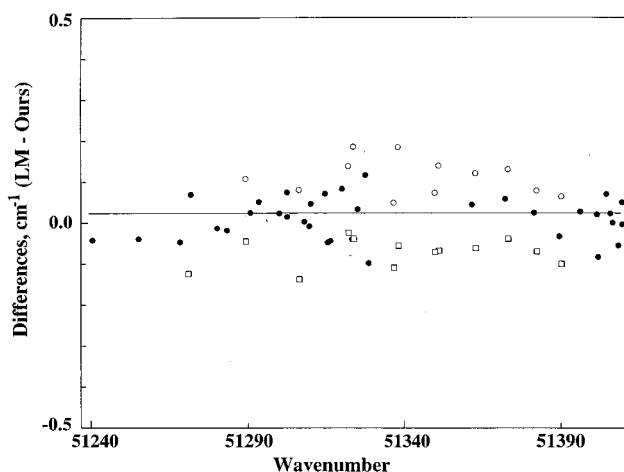


FIG. 2. Differences in the observed line positions of the  $\beta(6,0)$  band between our results and Lagerqvist and Miescher (Ref. 13). The differences are given by the solid circles. For the lines separated  $\Lambda$ -doubling in this work are given by the open circles and squares. The solid horizontal line represents the average shift of  $-0.019 \text{ cm}^{-1}$ .

## II. EXPERIMENT

Details of the experimental procedures for recording high resolution FT spectra of NO between 160–198 nm have been described in our earlier publications.<sup>1–3</sup> Only a brief description of the experimental conditions with respect to the recording of the  $\beta(6,0)$  and  $\gamma(3,0)$  bands will be given here. An absorption cell with optical path length of 7.54 cm was used, which was filled with 0.300 Torr of NO at 295 K. The column density of NO in this experiment was  $7.4 \times 10^{16} \text{ mol cm}^{-2}$ . A total of 236 scans, corresponding to above 10.7 hours of integration time, with a resolution of  $0.06 \text{ cm}^{-1}$ , have been co-added. The signal-to-noise ratio in the continuum background was about 50. The resonance line of Hg I at 184.8 nm was used as reference wave number in the previous papers.<sup>1,2</sup> However, in this wavelength region we have no convenient absolute reference. From the calibration constant in the previous papers, we estimate the uncertainty in the absolute values as  $0.02 \text{ cm}^{-1}$ . Relative uncertainties for the strong lines are better than  $0.01 \text{ cm}^{-1}$ .

## III. RESULTS AND DISCUSSION

The absorption spectra at around 195 nm were converted to optical depth by taking the logarithms of the intensity and fitting a smooth continuum to the regions between the lines. The absorption lines were fitted to Voigt profiles using the spectral reduction routine GREMLIN.<sup>20</sup> The Voigt profile for the NO lines is a convolution of a Gaussian line shape due to Doppler broadening and a Lorentzian line shape arising from predissociation. Line parameters are determined through a nonlinear least squares iterative procedure that takes as free parameters both the Gaussian and the Lorentzian contributions as well as the line center and integrated intensity. However, in the fitting to retrieve line parameter, Gaussian component is sufficient to describe the line shape, because the upper levels of these band systems are located below the dissociation energy. The fitted profiles yielded an anoma-

TABLE I. (a) Observed wave numbers of the  $\gamma(3,0)$  band of NO.<sup>a</sup> (b) Observed wave numbers of the  $\beta(6,0)$  band of NO.<sup>c</sup>

(a)								
$J$	$P_{11}$	$R_{11}+Q_{21}^b$	$P_{21}+Q_{11}^b$	$R_{21}$	$P_{22}+Q_{12}^b$	$R_{22}$	$P_{12}$	$R_{12}+Q_{22}^b$
0.5						51 018.459		
1.5	51 121.598	51 133.162	51 125.431	51 144.737	51 005.345	51 024.841	51 001.670	51 013.267
2.5	51 117.087	51 136.379	51 124.767	51 151.790	51 004.571	51 031.676B	50 996.939	51 016.247
3.5	51 113.097	51 140.127	51 124.675	51 159.366	51 004.173	51 038.928	50 992.613	51 019.628
4.5	51 109.640	51 144.367	51 125.013	51 167.470	51 004.173	51 046.590	50 988.712	51 023.455
5.5	51 106.689	51 149.146	51 125.929	51 176.084	51 004.571	51 054.688	50 985.226	51 027.676
6.5	51 104.253	51 154.410	51 127.327	51 185.204	51 005.345	51 063.201	50 982.162	51 032.350
7.5	51 102.328B	51 160.207	51 129.245	51 194.829	51 006.545	51 072.125	50 979.543	51 037.418
8.5	51 100.914	51 166.490	51 131.666	51 204.974	51 008.184	51 081.475	50 977.327	51 042.914
9.5	51 100.010	51 173.303	51 134.607	51 215.620	51 010.248	51 091.259	50 975.508	51 048.826
10.5	51 099.614B	51 180.625	51 138.078	51 226.759	51 012.734	51 101.423B	50 974.164	51 055.175
11.5	51 099.729B	51 188.435	51 142.032	51 238.431	51 015.648	51 112.051	50 973.222	51 061.928
12.5	51 100.368	51 196.752	51 146.491	51 250.590	51 018.995	51 123.081	50 972.717B	51 069.132
13.5	51 101.502B	51 205.593	51 151.481	51 263.265	51 022.756	51 134.545B	50 972.639B	51 076.753
14.5	51 103.144	51 214.931	51 156.950	51 276.435	51 026.965	51 146.430B	50 972.985B	51 084.804
15.5	51 105.290	51 224.766	51 162.952	51 290.090	51 031.606	51 158.747	50 973.772	51 093.262
16.5	51 107.950		51 169.437	51 304.251	51 036.644	51 171.457	50 974.968	51 102.281
17.5	51 111.102		51 176.415	51 318.935	51 042.146	51 184.639B	50 976.637	51 111.498
18.5	51 114.774		51 183.909	51 334.122	51 048.076	51 198.263		51 121.288
19.5			51 191.903	51 349.761B	51 054.425	51 212.255		
20.5			51 200.368			51 226.685		
21.5			51 209.362					
22.5			51 218.854					
23.5			51 228.810					
24.5			51 239.216					

(b)								
$I$	$R_{11}(J)_e$	$R_{11}(J)_f$	$P_{11}(J)_e$	$P_{11}(J)_f$	$Q_{11}(J)$	$R_{22}(J)$	$P_{22}(J)$	$Q_{22}(J)$
0.5	51 409.450				51 406.400			
1.5	51 409.504		51 401.380		51 404.430	51 328.599		51 323.241
2.5	51 408.256		51 396.073		51 401.139	51 327.484	51 314.629	51 320.017
3.5	51 405.677		51 389.434			51 325.067	51 307.998	51 315.449
4.5	51 401.784		51 381.476			51 321.365	51 299.977	51 309.609
5.5	51 396.035	51 396.167		51 372.242		51 316.345	51 290.676	51 302.486
6.5	51 390.036	51 390.201		51 361.656		51 310.054	51 280.114	
7.5	51 382.222	51 382.371	51 349.727	51 349.872		51 302.426	51 268.248	
8.5	51 373.070	51 373.240	51 336.551	51 336.710		51 293.449	51 255.040	
9.5	51 362.680	51 362.863	51 321.962	51 322.125		51 283.219	51 240.543	
10.5	51 350.961	51 351.169	51 306.220	51 306.438		51 271.631	51 224.709	
11.5	51 337.916	51 338.157	51 289.093	51 289.246		51 258.781	51 207.593	
12.5	51 323.615	51 323.840	51 270.085	51 270.925		51 244.584	51 189.139	
13.5	51 307.980	51 308.245	51 251.014	51 251.207		51 229.060	51 169.374	
14.5	51 291.114	51 291.343	51 229.982	51 230.226		51 212.256		
15.5	51 273.019	51 273.203	51 207.654	51 208.005		51 194.076		
16.5	51 253.401	51 253.738				51 174.602		
17.5						51 153.795		

<sup>a</sup>The uncertainty in the absolute values is  $0.02 \text{ cm}^{-1}$ , but the precision of the relative values is better than  $0.01 \text{ cm}^{-1}$  for all except the very weak lines.

<sup>b</sup>Transition line of the two branches are overlapped.

<sup>c</sup>The uncertainty in the absolute values is  $0.02 \text{ cm}^{-1}$ , but the precision of the relative values is better than  $0.01 \text{ cm}^{-1}$  for all except the very weak lines.

lously large Gaussian contribution, with a full width at half maximum (FWHM) of  $0.175 \text{ cm}^{-1}$ , as against the  $0.12 \text{ cm}^{-1}$  expected for Doppler width in our experimental conditions. This anomalous Gaussian width is considered to be due to drifts in alignment of the synchrotron beam and the external optics which cause very small wave number shifts over the long observation periods.<sup>21</sup>

### A. Line positions and molecular constants

Figure 1(A) shows the Fourier transform spectrum of the  $\beta(6,0)$  and  $\gamma(3,0)$  bands near 195 nm. As can be seen, the

$\beta(6,0)$  band is considerably weaker than the  $\gamma(3,0)$  band. The high  $J$  lines of the  $\gamma(3,0)$  band overlap heavily with the  $\beta(6,0)$  band. Figure 1(B) is an expanded portion of the spectrum showing details of the rotational structure of the  $\gamma(3,0)$  band. We observed 76 lines of the  $\beta(6,0)$  band and these lines were assigned to six main branches ( $P_1$ ,  $Q_1$ ,  $R_1$ ,  $P_2$ ,  $Q_2$ , and  $R_2$ ). For the  $\gamma(3,0)$  band, 224 lines belonging to 12 branches expected from a  ${}^2\Sigma^-2\Pi$  transitions have been assigned for the first time. These lines are tabulated in (a) and (b) of Table I. Lagerqvist and Miescher<sup>13</sup> had studied the

TABLE II. The term values of the  $A(3) \ ^2\Sigma^+$  and the  $B(6) \ ^2\Pi$  levels of NO,<sup>a</sup>  $\text{cm}^{-1}$ .

$J$	$A(3) \ ^2\Sigma^+$		$B(6) \ ^2\Pi$			
	$F_1(J)$	$F_2(J)$	$F_1(J)^2\Pi_{1/2}$		$F_2(J)^2\Pi_{3/2}$	
	$e$	$f$	$e$	$f$	$e$	$f$
0.5	51 126.596(10)	51 130.467(01)	51 406.40(2)	51 406.41(1)		
1.5	51 130.452(02)	51 138.178(01)	51 409.45(1)	51 409.46(2)	51 448.15(1)	51 448.15(1)
2.5	51 138.162(04)	51 149.758(12)	51 414.52(2)	51 414.53(2)	51 453.53(2)	51 453.53(2)
3.5	51 149.744(01)	51 165.190(01)	51 421.60(3)	51 421.65(1)	51 461.00(1)	51 461.00(1)
4.5	51 165.176(02)	51 184.482(09)	51 430.74(1)	51 430.79(1)	51 470.63(1)	51 470.63(1)
5.5	51 184.465(06)	51 207.632(04)	51 441.87(3)	51 442.03(1)	51 482.41(2)	51 482.42(2)
6.5	51 207.624(07)	51 234.639(07)	51 455.02(0)	51 455.24(3)	51 496.31(3)	51 496.31(3)
7.5	51 234.625(03)	51 265.505(05)	51 470.26(0)	51 470.48(2)	51 512.35(1)	51 512.35(1)
8.5	51 265.474(16)	51 300.209(04)	51 487.48(4)	51 487.73(3)	51 530.50(1)	51 530.51(1)
9.5	51 300.179(52)	51 338.783(03)	51 506.79(1)	51 507.10(4)	51 550.74(1)	51 550.75(1)
10.5	51 338.753(06)	51 381.205(08)	51 528.13(3)	51 528.42(3)	51 573.15(3)	51 573.15(3)
11.5	51 381.172(04)	51 427.454(09)	51 551.56(4)	51 551.87(1)	51 597.69(3)	51 597.70(3)
12.5	51 427.428(48)	51 477.584(04)	51 576.94(1)	51 577.30(1)	51 624.27(5)	51 624.28(5)
13.5	51 477.552(05)	51 531.545(08)	51 604.41(2)	51 604.79(0)	51 653.04(3)	51 653.05(3)
14.5	51 531.513(09)	51 589.358(08)	51 633.91(4)	51 634.37(4)	51 683.86(3)	51 683.87(3)
15.5	51 589.311(13)	51 651.008(08)	51 665.52(3)	51 665.91(3)	51 716.82(3)	51 716.83(3)
16.5	51 650.960(07)	51 716.499(16)	51 699.10(3)	51 699.60(3)	51 751.81(3)	51 751.83(3)
17.5	51 716.464(06)	51 785.810(10)	51 734.77(3)	51 735.29(3)	51 788.93(3)	51 788.95(3)
18.5	51 785.787(01)	51 858.992(17)			51 828.12(3)	51 828.14(3)
19.5	51 858.953(04)	51 936.005(16)				
20.5	51 935.936(15)	51 916.813(26)				
21.5	52 016.765(15)					

<sup>a</sup>The uncertainties shown are the standard deviations and refer to relative values. The uncertainty in the absolute values is  $0.02 \text{ cm}^{-1}$  (see text).

$\beta(6,0)$  band, and differences in the observed line positions (their values—our values) are plotted in Fig. 2. The agreement is excellent,  $+0.019 \pm 0.092 \text{ cm}^{-1}$ . Our measurements have extended the assignment of rotational lines to  $J=17.5$  of the  $\beta(6,0)$  band and  $J=21.5$  of the  $\gamma(3,0)$  band.  $\Lambda$ -doubling of the  $\beta(6,0)$  band has been observed in  $R_1$  and  $P_1$  branches.

The rotational term values of the  $v=6$  level of the  $B \ ^2\Pi_r$  state [upper state of the  $\beta(6,0)$  band] and  $v=3$  level of the  $A \ ^2\Sigma^+$  state [upper state of the  $\gamma(3,0)$  band] have been obtained by adding the term values of the  $v=0$  level of the  $X \ ^2\Pi_r$  state to the wave numbers of the observed transition lines. The ground state rotational term values used are those of Amiot *et al.*,<sup>22</sup> for which the relative zero was set at the

$\Omega=1/2$  and  $J=0.5$  level. The upper state term values obtained are averaged, and the results are listed in Table II, with the standard deviation shown as the uncertainty.

The effective Hamiltonian operator suitable for the description of the  $^2\Pi$  and  $^2\Sigma$  states can be found in Zare *et al.*<sup>23</sup> and Hougen.<sup>24</sup> The matrix elements used in this work for the calculation of rotational energy levels are the same as those in Amiot *et al.*<sup>26</sup> The parameters included in the description of the  $^2\Pi$  state are the band origin  $T_0$ ; the rotational parameters  $B$  and  $D$ ; the spin-orbit parameters  $A$  and  $A_D$ . For the  $^2\Sigma$  state: the band origin  $T_0$ ; the rotational parameters  $B$  and  $D$ ; the spin-rotation constant  $\gamma$ . The rovibronic term values of the upper state of the  $\beta(6,0)$  and  $\gamma(3,0)$  bands were fitted to the parameters of the  $^2\Pi$  and  $^2\Sigma$

TABLE III. Molecular parameters of the  $B \ ^2\Pi$   $v=6$  and  $A \ ^2\Sigma^+$   $v=3$  levels of NO ( $\text{cm}^{-1}$ ).<sup>a</sup>

	$B(6) \ ^2\Pi$		$A(3) \ ^2\Sigma^+$			
	This work	BM <sup>b</sup>	This work	DDKRZ <sup>c</sup>	ER <sup>d</sup>	GS <sup>e</sup>
$T_0^f$	51 425.67(1)	51425	51 126.60(1)	51 068.426		51 127.2
$B$	1.0415(3)	1.041	1.929 42(3)	1.929 482	1.9298	1.9290
$10^5 D$	0.44(3)		0.561(5)	0.571		
$A$	40.621(9)	40.6				
$A_D$	0.000 26(6)					
$p$	0.0283(8)					
$q$	-0.000 28(5)					
$\gamma$			-0.0025(2)	-0.002 77		

<sup>a</sup>Errors in parentheses are one standard deviation in units of the last significant figure quoted.

<sup>b</sup>BM: Barrow and Miescher (Ref. 25).

<sup>c</sup>DDKRZ: Danielak *et al.* (Ref. 12).

<sup>d</sup>ER: Engleman and Rouse (Ref. 11).

<sup>e</sup>GS: Gerö and Schmid (Ref. 9).

<sup>f</sup>The uncertainty in  $T_0$  is dominated by the  $0.02 \text{ cm}^{-1}$  uncertainty in absolute wave numbers.

TABLE IV. (a) Integrated cross sections of lines of the  $\gamma(3,0)$  band of NO in units of  $10^{-18} \text{ cm}^2 \text{ cm}^{-1}$ . (b) Integrated cross sections of lines of the  $\beta(6,0)$  band of NO in units of  $10^{-18} \text{ cm}^2 \text{ cm}^{-1}$ .<sup>b</sup>

$J$	(a)							
	$P_{11}$	$R_{11}+Q_{21}^a$	$P_{21}+Q_{11}^a$	$R_{21}$	$P_{22}+Q_{12}^a$	$R_{22}$	$P_{12}$	$R_{12}+Q_{22}^a$
0.5								
1.5	0.50	1.41	1.00	0.75	1.28	0.18	0.75	0.89
2.5	0.97	2.28	2.09	1.01	1.75	0.30	0.85	1.27
3.5	1.31	2.55	2.70	1.15	1.82	0.46	0.90	1.65
4.5	1.35	2.86	3.02	1.38	2.16	0.66	0.91	1.96
5.5	1.55	3.16	3.31	1.48	2.37	0.77	0.88	2.07
6.5	1.64	3.23	3.62	1.50	2.41	0.84	0.90	2.27
7.5	1.89	3.38	3.61	1.31	2.32	0.93	0.89	2.34
8.5	1.80	3.39	3.65	1.18	2.31	0.95	0.75	2.29
9.5	1.81	3.32	3.61	1.16	2.23	0.93	0.67	2.22
10.5	1.80	3.22	3.46	0.97	1.99	0.89	0.63	2.20
11.5	1.66	3.16	3.47	0.86	1.85	0.88	0.55	1.99
12.5	1.29	2.90	3.24	0.79	1.63	0.77	0.47	1.89
13.5	1.23	2.66	2.89	0.67	1.54	0.75	0.42	1.65
14.5	1.18	2.37	2.82	0.67	1.22	0.65	0.33	1.38
15.5	1.05	2.08	2.41	0.39	0.92	0.48	0.34	1.29
16.5	0.83	1.47	2.10	0.35	0.80	0.40	0.22	1.08
17.5	0.65		1.77	0.32	0.54	0.29	0.13	0.76
18.5	0.68		1.57	0.22	0.54	0.29		0.65
19.5			1.18	0.27	0.36			
20.5			0.99		0.26			
21.5			0.71		0.21			
22.5			0.51					
23.5			0.20					
Total	23.19	43.44	53.93	16.43	30.51	11.42	10.59	29.85
Extended	25.24	52.42	56.89	17.03	31.50	12.30	11.44	31.31

$J$	(b)							
	$R_{11}(J)_e$	$R_{11}(J)_f$	$P_{11}(J)_e$	$P_{11}(J)_f$	$Q_{11}(J)$	$R_{22}(J)$	$P_{22}(J)$	$Q_{22}(J)$
0.5		0.63			0.40			
1.5		0.76		0.39	0.20	0.35		0.33
2.5		1.12		0.54		0.42	0.14	0.20
3.5		1.16		0.71		0.36	0.35	
4.5	0.75	0.62		0.85		0.40	0.22	
5.5	0.61	0.52		0.87		0.58	0.49	
6.5	0.75	0.51	0.58	0.37		0.54	0.51	
7.5	0.59	0.44	0.62	0.45		0.43	0.56	
8.5	0.50	0.51	0.55	0.42		0.68	0.60	
9.5	0.54	0.53	0.47	0.43		0.62	0.63	
10.5	0.49	0.39	0.53	0.31		0.53	0.59	
11.5	0.41	0.47	0.29	0.28		0.51	0.34	
12.5	0.29	0.41	0.41	0.25		0.50	0.25	
13.5	0.31	0.31	0.30	0.29		0.37	0.10	
14.5	0.21	0.19	0.26	0.28		0.35		
15.5	0.13	0.23	0.29	0.21		0.14		
16.5	0.12	0.17						
Total		14.67		10.95	0.60	6.78	4.78	0.53
Extended		16.12		12.99	0.60	7.84	5.18	0.53

<sup>a</sup>Transition line of the two branches are overlapped. Total integrated cross section:  $219.36 \times 10^{-18} \text{ cm}^2 \text{ cm}^{-1}$ .  
 Extended integrated cross section:  $238.13 \times 10^{-18} \text{ cm}^2 \text{ cm}^{-1}$ .

<sup>b</sup>Transition line of the two branches are overlapped. Total integrated cross section:  $38.31 \times 10^{-18} \text{ cm}^2 \text{ cm}^{-1}$ .  
 Extended integrated cross section:  $42.56 \times 10^{-18} \text{ cm}^2 \text{ cm}^{-1}$ .

state, respectively. Using a least squares package, the molecular parameters obtained for the  $v=6$  level of the  $B^2\Pi_r$  state and the  $v=3$  of the  $A^2\Sigma^+$  state are listed in Table III. The molecular parameters determined by Engleman and Rouse,<sup>11</sup> Danielak *et al.*,<sup>12</sup> and Barrow and Miescher<sup>25</sup> are included for comparison. The apparent discrepancy between

the band origin measured in this work and that of Danielak *et al.*<sup>12</sup> arises from the use of different reference points in the  $X^2\Pi$  state. In the ground state term value calculation, Danielak *et al.*<sup>12</sup> used matrix elements in Table II of Amiot *et al.*,<sup>26</sup> which were different from those of Amiot *et al.*<sup>22</sup> by  $58.171 \text{ cm}^{-1}$ . This difference in term value is exactly equal

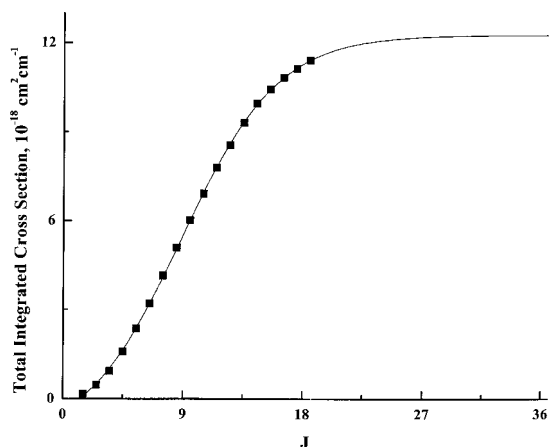


FIG. 3. Line by line total integrated cross-sections of the  $R_{22}$  branch of the  $\gamma(3,0)$  band.

to an amount  $-\frac{1}{2}A + 2B + \frac{1}{2}p$  as listed in the matrix elements. Our molecular parameters were determined with high accuracy and the agreement between our values and those of earlier work is excellent.

## B. Band oscillator strength

The band oscillator strengths are given by

$$f(v', v'') = \frac{mc^2}{\pi e^2} \frac{1}{\bar{N}(v'')} \int \sigma(v) dv, \quad (1)$$

where  $\bar{N}(v'')$  is the fractional Boltzmann population of the absorbing vibrational level, and the integration of the cross section is performed over all the rotational lines belonging to the  $(v', v'')$  band. In our retrieval of line parameters from the absorption spectrum, in addition to line positions, the integrated cross section of each line was also obtained. (a) and (b) of Table IV list the integrated cross sections of the rotational lines of these two bands. The integration of the cross sections of all observed rotational lines of the  $\gamma(3,0)$  and  $\beta(6,0)$  bands is equal to the sum of the integrated cross sections of all observed lines in (a) and (b) of Table IV, respectively. For the  $\beta(6,0)$  band, the weak satellite branches from this  $\Delta\Lambda = 0$  transition were not observed. It is expected that the contribution of these satellite branches to the band oscillator strength should be insignificant. Observations of rotational lines are mostly limited to  $J \leq 22.5$ . The contributions of the higher  $J$  lines are obtained by extending the total integrated cross sections to  $J = 36.5$ . Figure 3 is a plot of the total integrated cross sections of the  $R_{22}$  branch of the  $\gamma(3,0)$

band versus  $J$ . The solid line in the figure was obtained by fitting those experimental points and the extended contribution was estimated by extrapolating the line to  $J = 36.5$ . The results of the extended contributions are also listed in (a) and (b) of Table IV. Table V gives the band oscillator strengths determined for the  $\beta(6,0)$  and  $\gamma(3,0)$  bands. Errors in the band oscillator strengths obtained by integration over all lines are estimated to be about 10% for the  $\beta(6,0)$  band and 5% for the stronger  $\gamma(3,0)$  bands, including uncertainties from extrapolation as well as those in the measured lines. Table V compares our values with those in the literature. Among all the band oscillator strength determinations, only ours were performed using line by line measurement with a resolution comparable to the Doppler width of the spectral lines. We notice that our value of the  $\gamma(3,0)$  band is among the smallest of the published values, and suggest that our line by line measurement can identify accurately the transition lines belonging to the  $\gamma(3,0)$  band and exclude any overlapping transition intensity of other bands. Our determined value for the  $\beta(6,0)$  band is the largest among these values. We would like to postpone our discussion of band oscillator strengths of various band systems of NO in the wavelength region 160–195 nm until after the analyses of all these bands are completed.

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TABLE V. Band oscillator strength ( $10^{-4}$ ) of NO.

	$\gamma(3,0)$	$\beta(6,0)$
This work	2.69	0.48
Luque and Crosley (Ref. 19)	3.00	
Chan, Cooper, and Brion (Ref. 17)	3.6	0.37
Laux and Kruger (Ref. 18)	3.41	0.431
Cieslik (Ref. 16)	3.0	
Farmer, Hasson, and Nicholls (Ref. 15)	2.4	
Bethke (Ref. 14)	3.60	0.462

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