



<b>Title</b>	<b>Predissociation linewidths of the (3,0)-(11,0) Schumann-Runge absorption bands of 18O<sub>2</sub> and 16O 18O in the wavelength region 180-196 nm</b>
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# Predissociation linewidths of the (3,0)–(11,0) Schumann–Runge absorption bands of $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ in the wavelength region 180–196 nm

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Predissociation linewidths of the (3,0)–(11,0) Schumann–Runge bands of  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  in the wavelength region 180–196 nm have been obtained from the published measurements of the absolute absorption cross sections of Yoshino *et al.* [*Planet. Space Sci.* **36**, 1201 (1988); **37**, 419 (1989)] and spectroscopic constants of these molecules of Cheung *et al.* [*J. Mol. Spectrosc.* **131**, 96 (1988); **134**, 362 (1989)]. The linewidths are determined as parameters in the nonlinear least-squares fitting of calculated to measured cross sections. Predissociation maxima are found at upper vibrational levels with  $v' = 4, 7, \text{ and } 10$  for  $^{18}\text{O}_2$  and for  $^{16}\text{O}^{18}\text{O}$ . Our predissociation linewidths are mostly greater than previous experimental values for both isotopic molecules.

## I. INTRODUCTION

In a previous paper,<sup>1</sup> we determined the predissociation linewidths of the (1,0)–(12,0) Schumann–Runge bands of  $^{16}\text{O}_2$  from our measurements of the absolute absorption cross sections<sup>2,3</sup> and our spectroscopic constants<sup>4</sup> of these bands.<sup>5</sup> The Schumann–Runge absorption bands of  $^{16}\text{O}_2$  and their extensive predissociation are of considerable atmospheric significance in connection with the transmission of solar radiation and the production of  $\text{O}(^3P)$  atoms. The predissociation linewidths and, in particular, their variation with the upper-level vibrational quantum number  $v'$ , are also of importance in the elucidation of the curve-crossing mechanism<sup>6,7</sup> responsible for the predissociation. The analogous predissociation linewidths of the Schumann–Runge bands of  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  would provide valuable supplementary information on the mechanism of predissociation because the predissociating vibronic energy levels, but not the associated bound and repulsive potential-energy curves, are isotope dependent. In addition,  $^{16}\text{O}^{18}\text{O}$  constitutes about 0.4% of atmospheric  $\text{O}_2$  and is a source, via predissociation, of  $^{18}\text{O}$  in the stratosphere.<sup>8,9</sup>

In the present study, we use techniques similar to those we have employed<sup>1</sup> for  $^{16}\text{O}_2$  to deduce the predissociation linewidths of the (3,0)–(11,0) Schumann–Runge absorption bands of  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  from our recent measurements in the wavelength region 180–196 nm of the absolute absorption cross sections<sup>10,11</sup> and spectroscopic constants<sup>12,13</sup> of these molecules.

## II. PROCEDURE

In brief, an initial synthetic spectrum of the absorption cross section, calculated from line-center positions, line strengths, and line profiles, is adjusted by an iterative nonlinear least-squares procedure to procure a best fit between the measured and calculated cross sections by variation of the predissociation linewidths used to specify the line profiles.<sup>1</sup>

The line-center positions of the unresolved or partially resolved fine-structure components of the rotational lines are calculated from our experimental or interpolated spectroscopic constants derived from our high-resolution photographic wavelength measurements<sup>12,13</sup> on  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$ . The line strengths of the fine-structure components of a rotational line, involving products of Hönl–London factors and Boltzmann population factors, are calculated for  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  in the same way<sup>1</sup> as for  $^{16}\text{O}_2$ , except that for  $^{16}\text{O}^{18}\text{O}$  account is taken of the fact the ground-state levels with both even and odd values of the rotational quantum number  $N''$  are populated. The line profile of a fine-structure component of a rotational line of  $^{18}\text{O}_2$  or  $^{16}\text{O}^{18}\text{O}$  is described by a Lorentzian shape of which the width is taken to be the predissociation linewidth, and, just as in our treatment<sup>1</sup> of  $^{16}\text{O}_2$ , the smallness of the Doppler linewidth compared with the predissociation linewidths obviates the need for the use of Voigt line shapes. For the unresolved fine-structure components of a line, equal Lorentzian predissociation widths and constant relative line strengths are assumed during the fitting procedure. The assumption of equal predissociation widths for the fine-structure components of a line, made for lack of anything better, is a somewhat arbitrary constraint that avoids a multiplicity of solutions in the fitting of an unresolved profile containing three, or sometimes six, individual components. Initial estimates of the predissociation linewidths are refined iteratively in the fitting of the calculated to the measured cross sections. Band oscillator strengths are not used explicitly in the calculation.

Our measured cross sections<sup>10,11</sup> for  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$ , obtained at 79 K, permit the determination of predissociation linewidths of rotational features with upper-state rotational quantum number  $N'$  up to 12 or 14. Examples illustrating the quality of the fitting achieved are shown in Fig. 1 for the bandhead region of the (9,0) band of  $^{18}\text{O}_2$  at 79 K, and in Fig. 2 for a portion of the (9,0) band of  $^{16}\text{O}^{18}\text{O}$  at 79 K. In Figs. 1 and 2, the discrete points are the measured cross sections to which the uppermost curve is fitted by the least-squares procedure discussed above. The

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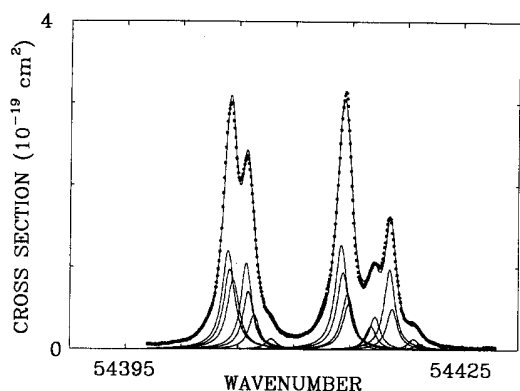


FIG. 1. Absorption cross section near the bandhead of the (9,0) Schumann-Runge band of  $^{18}\text{O}_2$  at 79 K. The uppermost curve is synthesized from the lower fine-structure component (Lorentzian) curves to fit the measured cross sections, represented by dots.

agreement between synthetic and experimental cross sections is good. The lower curves in Figs. 1 and 2 are the Lorentzian fine-structure components the sum of which yields the uppermost resultant synthetic cross section. Our measured cross sections of the complete (9,0) bands of  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  at 79 K are shown, respectively, in Fig. 1(h) of Ref. 10 and Fig. 2(g) of Ref. (11).

In Figs. 1 and 2, the spectral intervals over which the fitting is performed are  $\sim 30 \text{ cm}^{-1}$ . In other regions of the spectra, the intervals in which absorption features are fitted simultaneously vary, depending on the extent of line overlapping encountered. Spectral congestion is generally more acute for  $^{16}\text{O}^{18}\text{O}$  than for  $^{18}\text{O}_2$ , because  $^{16}\text{O}^{18}\text{O}$  possesses lines with odd and even values of the ground-state rotational quantum number  $N''$ , whereas  $^{18}\text{O}_2$  (like  $^{16}\text{O}_2$ ) possesses only odd  $N''$  lines. In cases where, unlike those shown in Figs. 1 and 2, an absorption feature at the end of a particular spectral interval overlaps seriously into a neighboring interval, the following modified procedure is adopted. The predissociation linewidths obtained for the end features are taken initially as provisional values which, however, are adequate to permit the determination of accurate linewidths

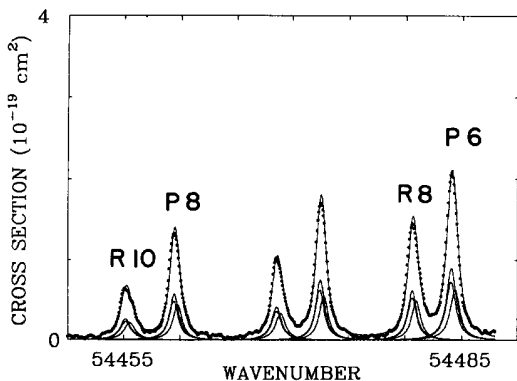


FIG. 2. Absorption cross section of a portion of the (9,0) Schumann-Runge band of  $^{16}\text{O}^{18}\text{O}$  at 79 K. The uppermost curve is synthesized from the lower fine-structure component (Lorentzian) curves to fit the measured cross sections, represented by dots.

in the central part of the spectral interval. Subsequently, adjacent spectral intervals are chosen so that the end features of the previous intervals are relocated in the central parts of the new intervals, enabling the previous provisional linewidth values to be refined in the fitting procedure.

### III. RESULTS AND DISCUSSION

Table I lists 114 predissociation linewidths [full width at half maximum (FWHM)] deduced from the absorption cross sections of the (3,0)–(11,0) bands of  $^{18}\text{O}_2$  at 79 K. Table II lists 186 predissociation linewidths (FWHM) deduced from the absorption cross sections of the (3,0)–(11,0) bands of  $^{16}\text{O}^{18}\text{O}$  at 79 K. In Tables I and II, linewidths are given for  $P$  and  $R$  branch lines and  $N'$  is the upper-state rotational quantum number, so that both lines of the same  $N'$  level can readily be compared. As in the case<sup>1</sup> of  $^{16}\text{O}_2$ , the results of the fitting procedure are not overly sensitive to the change of the linewidth, with the result that the scatter is fairly large.

In the bands (4,0)–(7,0) of  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$ , the rotational lines  $P(N'')$  and  $R(N'' + 2)$  happen to overlap each other so completely that only a single unresolved absorption feature is observed for most such pairs; in these cases, the six triplet components comprising the single measured feature are constrained, somewhat arbitrarily, in the fitting procedure, to have equal predissociation linewidths. Thus, in Tables I and II, the linewidths listed for  $P$  and  $R$  lines corresponding to  $N'$  and  $N' + 4$ , respectively, are mostly equal in the (4,0)–(7,0) bands. Similar overlapping occurs in the corresponding bands<sup>1</sup> of  $^{16}\text{O}_2$ .

We have examined our results in Tables I and II for possible evidence of the dependence of predissociation linewidth on rotational quantum number  $N'$ . The fact that our cross sections<sup>10,11</sup> for  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  are measure-

TABLE I. Predissociation linewidths ( $\text{cm}^{-1}$ , FWHM) of the Schumann-Runge bands ( $\nu', 0$ ) of  $^{18}\text{O}_2$  at 79 K.

$N'$	(3,0)		(4,0)		(5,0)		(6,0)		(7,0)	
	$P$	$R$	$P$	$R$	$P$	$R$	$P$	$R$	$P$	$R$
0	1.53		3.22		3.04		1.05		2.72	
2	1.67	1.29	3.31	3.22	3.22	3.04	1.08	1.05	2.98	2.72
4	1.51	1.53	3.26	3.22	3.22	3.04	1.05	1.05	2.73	2.72
6	1.57	1.37	3.19	3.31	3.15	3.22	1.04	1.08	2.67	2.98
8	1.35	1.65	3.04	3.26	3.09	3.22	0.99	1.05	2.68	2.73
10	1.80	1.68	3.39	3.19	3.03	3.15	1.08	1.04	2.86	2.67
12		1.45		3.04		3.09		0.99		2.68
14				3.39		3.03		1.08		2.86
$N'$	(8,0)		(9,0)		(10,0)		(11,0)			
	$P$	$R$	$P$	$R$	$P$	$R$	$P$	$R$		
0	1.29		1.29		1.60		0.78			
2	1.25	1.32	1.13	1.16	1.74	1.81	0.83	0.81		
4	1.70	1.29	1.23	1.29	1.75	1.60	0.84	0.78		
6	1.55	1.25	1.15	1.29	1.78	1.73	0.82	0.91		
8	1.52	1.04	1.15	1.15	1.75	1.72	0.88	0.88		
10	1.33	1.18	1.14	1.13	1.71	1.66	0.79	0.93		
12		1.17	1.09	1.09		1.68		0.86		
14			1.21							

TABLE II. Predissociation linewidths ( $\text{cm}^{-1}$ , FWHM) of the Schumann–Runge bands ( $v',0$ ) of  $^{16}\text{O}^{18}\text{O}$  at 79 K.

$N'$	(3,0)		(4,0)		(5,0)		(6,0)		(7,0)	
	$P$	$R$	$P$	$R$	$P$	$R$	$P$	$R$	$P$	$R$
0	1.74				2.52		1.32		2.21	
1	1.42	1.33			2.50	2.59	1.31	1.15	2.56	2.01
2	1.46	1.33	3.56		2.68	2.59	1.29	1.15	2.48	2.01
3	1.67	1.33	3.66		2.67	2.59	1.32	1.15	2.67	2.58
4	1.64	1.74	4.05		2.67	2.52	1.31	1.32	2.46	2.21
5	1.68	1.40	3.62		2.74	2.50	1.31	1.31	2.48	2.56
6	1.83	1.57	3.45	3.56	2.90	2.68	1.29	1.29	2.53	2.48
7	1.82	1.66	3.79	3.66	2.87	2.67	1.32	1.32	2.43	2.67
8		1.66	3.56	4.05	2.75	2.67	1.52	1.31	2.44	2.46
9		1.93	3.80	3.62		2.74	1.47	1.31	2.79	2.48
10		1.94		3.45		2.90		1.29		2.53
11				3.79		2.87		1.32		2.43
12				3.56		2.75		1.52		2.44
13				3.80				1.47		2.79
$N'$	(8,0)		(9,0)		(10,0)		(11,0)			
	$P$	$R$	$P$	$R$	$P$	$R$	$P$	$R$	$P$	$R$
0	1.34		0.94		1.76		1.37			
1	1.89	1.38	1.13	0.99	1.83	1.63	1.03	1.18		
2	1.98	1.38	0.99	0.99	1.59	1.63	0.96	1.18		
3	1.76	1.69	1.01	1.00	1.54	1.70	1.17	1.49		
4	1.67	1.34	1.02	0.94	1.73	1.76	1.20	1.37		
5	1.68	1.89	0.97	1.16	1.62	1.65	1.26	1.37		
6	1.57	1.52	0.92	0.95	1.71	1.73	1.28	1.49		
7	1.87	1.52	0.95	0.99	1.59	1.61	1.36	1.54		
8	1.70	1.59	1.03	0.88	1.69	1.52	1.28	1.45		
9		1.38		0.95		1.58	1.43	1.41		
10		1.88		1.06		1.67		1.47		
11		1.53		1.10		1.63		1.64		
12		1.53				1.93		1.63		
13						1.56				

ments at 79 K restricts the linewidth determinations to relatively low values of  $N'$  ( $N' < 14$ ), and, for the (4,0)–(7,0) bands, the above-mentioned constraint introduced to deal with the overlapping  $P$  and  $R$  branches further limits the amount of useful information obtainable on the variation of linewidth with upper-state rotational excitation. We have fitted the linewidths  $\Gamma$  for each band in Tables I and II to the formula  $\Gamma = \Gamma_0 + \alpha N'(N' + 1)$ , in which  $\Gamma_0$  is the rotationless width and  $\alpha$  expresses the rotational dependence. Inspection of the plots (not shown) of  $\Gamma$  vs  $N'$ , and of the values of  $\alpha/\Gamma_0$ , leads to the following conclusions. For  $^{18}\text{O}_2$ , changes of  $\Gamma$  with  $N'$  are slight, if any, for  $v' = 4$ –7 and 10; small apparent increases of  $\Gamma$  with  $N'$  may occur for  $v' = 3$  and 11, and small apparent decreases for  $v' = 8$  and 9. For  $^{16}\text{O}^{18}\text{O}$ , changes of  $\Gamma$  with  $N'$  are slight, if any, for  $v' = 4, 8, 9$ , and 10; small apparent increases of  $\Gamma$  with  $N'$  may occur for  $v' = 5$ –7, and larger apparent increases for  $v' = 3$  and 11. The foregoing inferences about the variation with rotational quantum number are tentative. For the bands of  $^{18}\text{O}_2$  with  $v' = 3$ –7 and 10, and for  $^{16}\text{O}^{18}\text{O}$  with  $v' = 4, 8, 9$ , and 10, our values of  $\alpha$  possess dubious significance, having uncertainties that equal or exceed their magnitude. Only a brief comparison with the results of Lewis, Berzins, and Carver,<sup>14,15</sup> which are based on measurements of equivalent widths for  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$ , seems warranted.

TABLE III. Comparison of present and previous linewidths ( $\text{cm}^{-1}$ , FWHM) for the (3,0)–(11,0) Schumann–Runge bands of  $^{18}\text{O}_2$ .

$v'$	Present <sup>a</sup>	Lewis <i>et al.</i> <sup>b</sup> (1987)	Julienne <sup>c</sup> (1976)
3	$1.53 \pm 0.15$	1.16	1.1
4	$3.23 \pm 0.11$	2.88	2.7
5	$3.12 \pm 0.08$	3.18	2.3
6	$1.05 \pm 0.03$	0.75	1.2
7	$2.77 \pm 0.11$	2.88	3.2
8	$1.32 \pm 0.18$	1.15	2.0
9	$1.18 \pm 0.07$	1.00	0.70
10	$1.71 \pm 0.07$	1.60	1.7
11	$0.84 \pm 0.05$	0.67	1.1

<sup>a</sup> Values obtained by averaging all data in Table I.

<sup>b</sup> Values extrapolated to zero rotation; from Table 1 of Lewis, Berzins, and Carver (Ref. 14).

<sup>c</sup> Calculated values; estimated from Fig. 10 of Julienne (Ref. 7).

For  $^{18}\text{O}_2$ , we and Lewis, Berzins, and Carver,<sup>14</sup> agree on the trends of linewidths with upper-state rotational excitation for  $v' = 3, 7, 9$ , and 11, but not for  $v' = 4$ –6 and 8. For  $^{16}\text{O}^{18}\text{O}$ , we and Lewis, Berzins, and Carver<sup>15</sup> agree for  $v' = 4, 6, 9$ , and 11, but not for  $v' = 3, 5, 7, 8$ , and 10.

In Tables III and IV, our predissociation linewidths are compared with others. Our values are averages (with  $1\sigma$  uncertainties) for each band of all the linewidths listed for that band in Table I or II; the values of Julienne<sup>7</sup> for  $^{18}\text{O}_2$  and Blake, Gibson, and McCoy<sup>8</sup> for  $^{16}\text{O}^{18}\text{O}$  are calculated results; and the experimental determinations of Lewis, Berzins, and Carver<sup>14,15</sup> for  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  are derived from a detailed modeling scheme in which predissociation linewidths and band oscillator strengths are simultaneously adjusted in the fitting of calculated to observed equivalent widths of rotational features measured with a 2.2 m scanning monochromator. Plots of the predissociation linewidths vs  $v'$ , from Tables III and IV, are presented in Figs. 3 and 4, respectively, for  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$ .

For  $^{18}\text{O}_2$ , the three sets of linewidths in Table III and Fig. 3 exhibit similar, but not identical, patterns of variation

TABLE IV. Comparison of present and previous linewidths ( $\text{cm}^{-1}$ , FWHM) for the (3,0)–(11,0) Schumann–Runge bands of  $^{16}\text{O}^{18}\text{O}$ .

$v'$	Present <sup>a</sup>	Lewis <i>et al.</i> <sup>b</sup> (1987)	Blake <i>et al.</i> <sup>c</sup> (1984)
3	$1.62 \pm 0.20$	1.57	1.25
4	$3.69 \pm 0.18$	3.76	2.80
5	$2.68 \pm 0.13$	2.61	2.02
6	$1.32 \pm 0.10$	1.15	1.39
7	$2.47 \pm 0.20$	2.28	2.03
8	$1.62 \pm 0.20$	1.38	1.19
9	$1.00 \pm 0.07$	0.67	0.67
10	$1.67 \pm 0.10$	1.22	1.05
11	$1.34 \pm 0.18$	0.87	0.97

<sup>a</sup> Values obtained by averaging all data in Table II.

<sup>b</sup> Values extrapolated to zero rotation; from Table I of Lewis, Berzins, and Carver (Ref. 15).

<sup>c</sup> Calculated values; estimated from Fig. 4 of Blake, Gibson, and McCoy (Ref. 8).

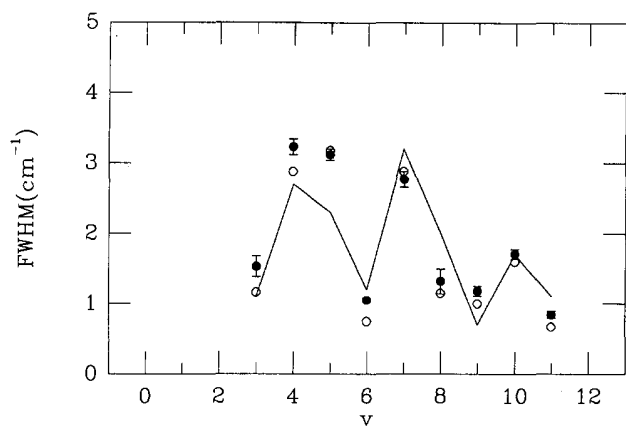


FIG. 3. Variation of predissociation linewidth with vibrational quantum number in the  $B^3\Sigma_u^-$  state of  $^{18}\text{O}_2$ . Solid circles: present average values; open circles: values of Lewis, Berzins, and Carver (Ref. 14); solid line: values of Julienne (Ref. 7).

with  $v'$ . We find the largest linewidths for  $v' = 4$  and the next largest for  $v' = 5$  (though the difference is only  $0.11 \text{ cm}^{-1}$ ) whereas Lewis, Berzins, and Carver<sup>14</sup> find this order reversed, and Julienne<sup>7</sup> calculates the largest linewidth for  $v' = 7$ . Compared with the linewidths of Lewis, Berzins, and Carver,<sup>14</sup> our values are greater for  $v' = 3, 4, 6,$  and  $8-11$  and only slightly smaller for  $v' = 5$  and  $7$ . In the simultaneous determination of linewidths and band oscillator strengths from equivalent widths, which is the method of Lewis, Berzins, and Carver,<sup>14</sup> a systematic error is possible arising from the inverse correlation between linewidth and oscillator strength in the computation of the equivalent width. For the  $(3,0)-(11,0)$  bands of  $^{18}\text{O}_2$ , the mean value of the ratios of the rotationless linewidths of Lewis, Berzins, and Carver<sup>14</sup> to our rotationless linewidths is 0.87, whereas the mean value of the rotationless band oscillator strengths of Lewis, Berzins, and Carver<sup>16</sup> to our band oscillator strengths<sup>10</sup> measured at 79 K is 1.18; this result suggests, but does not prove, that such a systematic error may be present

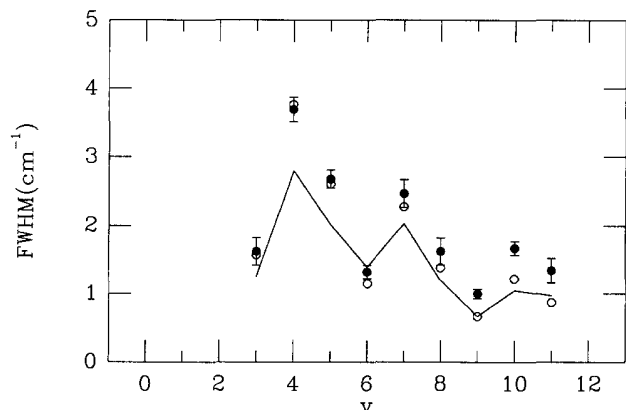


FIG. 4. Variation of predissociation linewidth with vibrational quantum number in the  $B^3\Sigma_u^-$  state of  $^{16}\text{O}^{18}\text{O}$ . Solid circles: present average values; open circles: values of Lewis, Berzins, and Carver (Ref. 15); solid line: values of Blake, Gibson, and McCoy (Ref. 8).

in the linewidths<sup>14</sup> and oscillator strengths<sup>16</sup> found for these bands by Lewis, Berzins, and Carver.

For  $^{16}\text{O}^{18}\text{O}$ , the three sets of linewidths in Table IV and Fig. 4 exhibit quite similar patterns of variation with  $v'$ . For  $v' = 3-8$ , the rotationless linewidths of Lewis, Berzins, and Carver<sup>15</sup> are in fair agreement with our values. For  $v' = 9-11$ , their rotationless linewidths are, on average,  $\sim 30\%$  smaller than ours; we note that their rotationless band oscillator strengths<sup>17</sup> for the  $(3,0)-(11,0)$  bands of  $^{16}\text{O}^{18}\text{O}$  are in satisfactory agreement with our band oscillator strengths<sup>11</sup> measured at 79 K, and the smallness of the linewidths of Lewis, Berzins, and Carver for the  $(9,0)-(11,0)$  bands of  $^{16}\text{O}^{18}\text{O}$ , relative to our values, remains unexplained.

Of the 30 bands we have studied for  $^{16}\text{O}_2$  ( $v' = 1-12$ ),  $^{18}\text{O}_2$  ( $v' = 3-11$ ), and  $^{16}\text{O}^{18}\text{O}$  ( $v' = 3-11$ ), we find rotationless linewidth values  $\Gamma_0 \geq 1.5 \text{ cm}^{-1}$  in 17 bands and  $\Gamma_0 < 1.5 \text{ cm}^{-1}$  in 13 bands. For the broader bands ( $\Gamma_0 \geq 1.5 \text{ cm}^{-1}$ ), the  $\Gamma_0$  values of Lewis, Berzins, and Carver are, on average,  $\sim 8\%$  lower than ours, whereas for the narrower bands ( $\Gamma_0 < 1.5 \text{ cm}^{-1}$ ), the  $\Gamma_0$  values of Lewis, Berzins, and Carver are, on average,  $\sim 25\%$  lower than ours.

The uncertainties associated with our average linewidths in Tables III and IV reflect the quality of the least-squares fitting of the measured cross sections, errors in the measured cross sections, possible errors in the assumed equality of the fine-structure component widths of a rotational line, uncertainties in the calculated line-center positions of the fine-structure components, and systematic variation (if any) of linewidth with upper-state rotational quantum number.

The most complete theoretical study of the mechanism of the predissociation of the Schumann-Runge bands of  $\text{O}_2$  is that of Julienne and Krauss<sup>6</sup> and Julienne,<sup>7</sup> who conclude that, of the four repulsive states ( $^5\Pi_u$ ,  $^3\Pi_u$ ,  $^1\Pi_u$ , and  $^3\Sigma_u^+$ ) contributing to the predissociation of the  $B^3\Sigma_u^-$  state in its bound region, the  $^5\Pi_u$  state produces the dominant effects on level shifts and level broadenings. For the  $^5\Pi_u-B^3\Sigma_u^-$  interaction, the ratio of the predissociation linewidths of the triplet components of a rotational line is predicted<sup>6,7</sup> to be close to 1:1:1. The general applicability of our empirical assumption, of equal widths for the triplet components of a line, to the extraction of predissociation linewidths from our cross-section data for  $^{16}\text{O}_2$ ,  $^{18}\text{O}_2$ , and  $^{16}\text{O}^{18}\text{O}$  is consistent with the theoretically predicted dominance of the  $^5\Pi_u-B^3\Sigma_u^-$  interaction. Nonetheless, an indication that our assumption may have limited validity is evident in the unsatisfactory fitting of the cross sections of lines with  $N'' \geq 11$  in the  $(9,0)$ ,  $(11,0)$ , and  $(12,0)$  bands<sup>1</sup> of  $^{16}\text{O}_2$  at 295 K; we observe no analogous indications in the bands of  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$ , possibly because those cross-section measurements at 79 K only are restricted to  $N'' \leq 13$ . We have also produced<sup>13</sup> a smooth deperturbation of the second vibrational energy differences for  $v' = 3-12$  for  $^{16}\text{O}_2$ ,  $^{18}\text{O}_2$ , and  $^{16}\text{O}^{18}\text{O}$  by use of a single set of the three model parameters (spin-orbit matrix element, curve-crossing point, and repulsive curve gradient at the crossing point) for the  $^5\Pi_u-B^3\Sigma_u^-$  interaction alone.

Lewis *et al.* have applied the predissociation model of

Julienne and Krauss<sup>6</sup> and Julienne<sup>7</sup> to their own linewidth determinations<sup>14,15,18</sup> for  $^{16}\text{O}_2$ ,  $^{18}\text{O}_2$ , and  $^{16}\text{O}^{18}\text{O}$ . Lewis *et al.* treat each isotopic molecule separately, and include the three model parameters for interactions with each of the four repulsive states. Thus, for each isotopic molecule, they find a different set of the twelve model parameters. In agreement with the theoretical predictions,<sup>6,7</sup> they conclude that the  $^5\Pi_u-B^3\Sigma_u^-$  interaction is strongest and that the  $^3\Sigma_u^+-B^3\Sigma_u^-$  interaction contributes significantly to the level broadenings for  $v' > 6$ .

#### IV. CONCLUDING REMARKS

Predissociation linewidths of the (3,0)–(11,0) Schumann–Runge bands of  $^{18}\text{O}_2$  and  $^{16}\text{O}^{18}\text{O}$  in the wavelength region 180–196 nm have been obtained from our published measurements of the absolute absorption cross sections and spectroscopic constants of these molecules. The linewidths are determined as parameters in the nonlinear least-squares fitting of calculated to measured cross sections. Predissociation maxima are found at upper-state vibrational quantum numbers  $v' = 4, 7, \text{ and } 10$  for  $^{18}\text{O}_2$  and for  $^{16}\text{O}^{18}\text{O}$ . Our predissociation linewidths are mostly greater than the recent experimental values of Lewis *et al.*<sup>14,15,18</sup> for  $^{18}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$ , and  $^{16}\text{O}_2$ .

Our assumption of equal predissociation linewidths for the fine-structure components of a rotational line is, for lines with rotational quantum numbers  $N'' < 11$ , consistent with the theoretical calculation of Julienne and Krauss<sup>6</sup> and Julienne<sup>7</sup> predicting the dominant influence of the repulsive  $^5\Pi_u$  state on the broadening of the vibronic levels of the  $B^3\Sigma_u^-$  state in its bound region. We have work in progress to improve the fitting of the cross sections of the (9,0), (11,0), and (12,0) bands of  $^{16}\text{O}_2$  at 295 K, by using different predissociation widths for the triplet components of a line. Our objective is to produce a single set of model parameters that fit simultaneously our predissociation linewidths and second vibrational differences for the Schumann–Runge absorption bands of the three isotopic molecules  $^{16}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$ , and  $^{18}\text{O}_2$ .

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