Title	Rotational dependence of the predissociation linewidths of the Schumann-Runge bands of O2
Author(s)	Cheung, ASC; Mok, DKW; Jamieson, MJ; Finch, M; Yoshino, K; Dalgarno, A; Parkinson, WH
Citation	The Journal Of Chemical Physics, 1993, v. 99 n. 2, p. 1086-1092
Issued Date	1993
URL	http://hdl.handle.net/10722/147714
Rights	Creative Commons: Attribution 3.0 Hong Kong License

Rotational dependence of the predissociation linewidths of the Schumann–Runge bands of O_2

A. S-C. Cheung[a] and D. K-W. Mok
Department of Chemistry, University of Hong Kong, Hong Kong

M. J. Jamieson,[b] M. Finch,[c] K. Yoshino, A. Dalgarno, and W. H. Parkinson
Harvard–Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138

(Received 22 February 1993; accepted 5 April 1993)

The predissociation linewidths of vibrational levels $v=0-12$ for $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ molecules in the $B\,^3\Sigma_u^-$ state with rotational quantum numbers $N\leqslant 20$ have been calculated taking into account the spin–orbit interactions of the $B\,^3\Sigma_u^-$ state with the $^5\Pi_u$, $^3\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$ states, and the rotational coupling with the $^3\Pi_u$ state. The predissociation linewidths exhibit systematic variations with rotational quantum number for different vibrational levels. Good agreement between most of the calculated and experimental linewidths has been obtained for all three isotopic molecules, with the exception of the set of linewidths of $^{16}O_2$ for $v=0$ and 2. The agreement can be improved by adjustment of the $^1\Pi_u$ potential and the strength of the spin–orbit interaction between the $B\,^3\Sigma_u^-$ and $^1\Pi_u$ states.

I. INTRODUCTION

The Schumann–Runge (SR) bands ($B\,^3\Sigma_u^- - X\,^3\Sigma_g^-$) of O_2 are of considerable interest in atmospheric chemistry and molecular physics because the $B\,^3\Sigma_u^-$ state undergoes predissociation to produce two $O(^3P)$ oxygen atoms.[1] Extensive experimental and theoretical studies have been performed to understand its predissociation.[2–20] It has been shown[4,5] that the predissociation is dominated by the interaction with the $^5\Pi_u$ state with lesser roles being played by the $^3\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$ states through spin–orbit coupling. In addition, the rotational coupling (orbit–rotation coupling) between the bound $B\,^3\Sigma_u^-$ state and the repulsive $^3\Pi_u$ state has been demonstrated by Yang *et al.*[18] to be important by their analysis of the dispersed laser-induced fluorescence spectra of high rotational lines of the (10,2) and (11,2) bands of the SR system.

The rotational dependence of predissociation depends on the mechanism responsible for the predissociation. The predissociation induced by rotational coupling exhibits linewidths increasing monotonically with rotational quantum number N,[19] while predissociation caused by spin–orbit coupling may result in an increase or decrease in linewidths as N increases.[4,5] In the $B\,^3\Sigma_u^-$ state of O_2, both rotational and spin–orbit couplings are important and the rotational variation of linewidths results from a combination of them.

In a previous paper,[20] we reported a single set of parameters characterizing the repulsive potentials of the states that interact with the $B\,^3\Sigma_u^-$ state through spin–orbit coupling and we described calculations of the predissociation linewidths for various vibration levels with N equal to zero. Here we estimate the rotational coupling constant theoretically and calculate the predissociation linewidths including both the spin–orbit and rotational couplings with rotational quantum number N up to 20.

II. THEORETICAL METHOD

The calculation of the predissociation linewidths has been described in detail in the earlier paper[20] and only a brief outline is given here. The predissociation of the $B\,^3\Sigma_u^-$ state was described in terms of its interactions with the four repulsive states $^5\Pi_u$, $^3\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$ through spin–orbit coupling. The $B\,^3\Sigma_u^-$ state potential was taken from Friedman.[21] For the repulsive potentials we adopted the form[4]

$$V(R)=V_x\exp[-(M_x/V_x)(R-R_x)], \tag{1}$$

where R denotes the internuclear distance, V_x and M_x are the energies and slopes at the crossing point, R_x, and the potential energy is measured from the $O(^3P)+O(^3P)$ energy of the repulsive states at infinite separation. The spin–orbit coupling matrix element is denoted by a constant A_x. We calculated the widths by the Fermi golden rule. The predissociation width due to a single curve crossing is proportional to the square of the product of A_x and the overlap of the wave functions of the bound and unbound states at the vibrational level of interest.[4,5] We solved the equations (in atomic units)

$$\left[-\frac{d^2}{dR^2}+2\mu V_B(R)+\frac{N(N+1)}{R^2}-2\mu E_{vN}\right]f_{vN}(R)=0, \tag{2}$$

$$\left[-\frac{d^2}{dR^2}+2\mu V_C(R)+\frac{N(N+1)}{R^2}+k^2\right]f_{kN}(R)=0, \tag{3}$$

to obtain the radial parts $f_{vN}(R)/R$ and $f_{kN}(R)/R$ of the initial bound vibrational state ($B\,^3\Sigma_u^-$) and final continuum state respectively for each channel ($^5\Pi_u$, $^3\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$). The potentials, referred to their own asymptotes, are denoted by $V_B(R)$ and $V_C(R)$, respectively, μ is the reduced mass, v and N are the vibrational and rotational

[a] International Exchange Scholar, Smithsonian Institution 1990–1992.
[b] Permanent address: Department of Computing Science, University of Glasgow, Glasgow G12 8QQ, Scotland.
[c] Present address: Department of Physics, Georgia Institute of Technology, Atlanta, Georgia.

 0021-9606/93/99(2)/1086/7/$6.00

angular momentum quantum numbers, respectively, and the energy, E_{vN}, of the bound state is related to the wave number, k, of the continuum state by

$$k^2=2\mu(\Delta E+E_{vN}), \tag{4}$$

where ΔE is the asymptotic separation of the predissociated and predissociating channels given, in this case, by the energy difference of $O(^1D)$ and $O(^3P)$ atoms. According to the golden rule, the width is

$$\Gamma=2\pi|\langle f_{vN}|\hat{H}_{\rm int}|f_{kN}\rangle|^2, \tag{5}$$

where the bound state is normalized to unity, the continuum state is energy normalized (asymptotic amplitude $[2/(\pi k)]^{1/2}$) and $\hat{H}_{\rm int}$ is the interaction causing predissociation. The interactions between the four final states were ignored. For small values of N the dominant predissociation mechanism is spin–orbit coupling.[4] We adopted the parameters describing the potentials (1) and the spin–orbit couplings which were previously determined by Chiu *et al.*[20] There is an additional coupling between the $B\,^3\Sigma_u^-$ and $^3\Pi_u$ states caused by rotational coupling, sometimes called Coriolis or l uncoupling.[4,18,19] Yang *et al.*[18] determined from observations of rotational levels N up to 30, rotational coupling matrix elements $[2N(N+1)]^{1/2}\eta$ with values for η of $(6.19\pm1.87)\times10^{-3}$ cm$^{-1/2}$ (these units were chosen to make the unit of width be cm^{-1}) and $(7.79\pm2.21)\times10^{-3}$ cm$^{-1/2}$ for the $v=10$ and 11 vibrational levels of the $B\,^3\Sigma_u^-$ channel, respectively. We estimated η using the hypothesis of pure precession. Note that the definition of the coupling matrix element given above absorbs a factor of $\sqrt{2}$. The η is the phenomenological coupling constant defined by Yang *et al.*[18] (in their Appendix) and

$$\eta=\langle f_{vN}|1/(2\mu R^2)|f_{kN}\rangle. \tag{6}$$

We obtained values of 6.23×10^{-3} cm$^{-1/2}$ and 5.63×10^{-3} cm$^{-1/2}$ for $v=10$ and 11, in reasonable agreement with the observations of Yang *et al.*[18] Most of the integral (6) comes from the Franck–Condon region and η is nearly directly proportional to the overlap integral $\langle f_{vN}|f_{kN}\rangle$. The spin–orbit matrix element ξ, defined by Julienne and Krauss,[4] is also proportional to the overlap integral so that the ratio $r=\eta/\xi$ is nearly independent of the vibrational quantum number v. Indeed, using the value of ξ obtained from the analysis of the widths of the $N=0$ lines by Chiu *et al.*,[20] we find by explicit evaluation of the integral (6) a value r of 0.0287 for $v=0$ increasing to 0.0296 for $v=11$.

The ratio, r, may be positive or negative. Lefebvre–Brion and Field[19] have expressed the widths of the individual fine-structure components arising from spin–orbit and rotational coupling to the $^3\Pi_u$ state in terms of ξ and η. The analysis in Yang *et al.*[18] of the widths suggest that r is a positive quantity.

The average width, taking into account the interaction with all four repulsive states, is given by Julienne[5]

$$\Gamma_{\rm avg}=\tfrac{20}{21}\Gamma(^5\Pi_u)+\tfrac{2}{3}\Gamma(^3\Sigma_u^+)+\tfrac{4}{3}\Gamma(^3\Pi_u)+\tfrac{2}{3}\Gamma(^1\Pi_u), \tag{7}$$

where the Γ's are the F_2 widths.

TABLE I. Potential parameters for the interactions with the $B\,^3\Sigma_u^-$ state.

(a)	State	$^5\Pi_u$	$^3\Sigma_u^+$	$^3\Pi_u$	$^1\Pi_u$
	A_x (cm^{-1})	70	46	35	33
	R_x(Å)	1.879	1.999	1.429	1.711
	M_x(cm^{-1} Å^{-1})	38 600	49 000	74 000	25 000
(b)	State	$^5\Pi_u$	$^3\Sigma_u^+$	$^3\Pi_u$	$^1\Pi_u$
	A_x(cm^{-1})	70	46	35	41
	R_x(Å)	1.879	1.999	1.429	1.730
	M_x (cm^{-1} Å^{-1})	38 600	49 000	74 000	25 000

Our data do not resolve the individual fine-structure components. From Table II of Yang *et al.*[18] and the results of Lefebvre–Brion and Field,[19] we must replace $\Gamma(^3\Pi_u)$ in Eq. (7) by

$$\Gamma(^3\Pi_u)=2\pi\xi^2\left[1+\left\{\frac{3}{2}N(N+1)-1\right\}r^2+\frac{r}{\sqrt{2}}\right]. \tag{8}$$

The terms in Eq. (8) include N-independent contributions when l uncoupling is incorporated, which changes the calculated values slightly for $N=0$. The ratio r varies little with N and the ratio of the contributions to the width from the rotational and spin–orbit couplings is approximately $[(N+\frac{1}{2})/(28+\frac{1}{2})]^2$, consistent with the suggestion of Julienne and Krauss[4] that rotational coupling would contribute for $N\geqslant10$. Table I(a) lists the 12 repulsive curve parameters A_x, R_x, and M_x determined previously.[20] These parameters have been used to calculate the full set of partial widths from Eq. (8). Table I(b) contains an alternative set of parameters for the $^1\Pi_u$ potential and spin–orbit interaction which we discuss below.

III. RESULTS AND DISCUSSION

In Tables II–IV we present, for $v=0$–12 and for N up to 20, the partial width due to each repulsive state, the total F_2 width, $\Gamma(F_2)$, and the average width, $\Gamma_{\rm avg}$, of the three F_i components for $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ calculated from the parameters of Table I(a). In Table II we include similar results but calculated with the parameters of Table I(b).

Vibrational levels $v=6$, 9, 11, 12 of $^{16}O_2$ were found to exhibit systematic variations of predissociation linewidths with rotational quantum number N.[15] Figures 1(a)–1(c) compare the calculated and experimental predissociation widths for $v=6$, 9, and 12. The agreement is excellent between experiment and theory for the parameters of Table I(a). Figure 1(d) shows the calculated and experimental linewidths for $v=11$. The calculated linewidths increase and finally level off as N increases whereas the experimental values of Cheung *et al.*[15] show a definite trend to increase. Cheung *et al.*[15] have reported difficulties in synthesizing the spectral profiles for $N>10$ and the linewidths retrieved are subject to larger uncertainties as N increases. Work to achieve more realistic synthesized profiles for these bands is in progress. For vibrational levels $v=5$, 7, and 10 of $^{16}O_2$, the calculated linewidths decrease as N increases and the agreement with experiment is satisfac-

TABLE II. Calculated widths in cm^{-1} for $^{16}O_2$. [(a): Parameters from Table I(a) (b): Parameters from Table I(b)].

v	N	$^5\Pi_u$	$^3\Sigma_u^+$	$^3\Pi_u$	$^1\Pi_u$(a)	$^1\Pi_u$(b)	$\Gamma(F_2)$(a)	$\Gamma(F_2)$(b)	Γ_{avg}(a)	Γ_{avg}(b)
0	0	0.000	0.000	0.013	0.289	0.194	0.302	0.206	0.209	0.146
0	5	0.000	0.000	0.013	0.292	0.197	0.305	0.209	0.212	0.148
0	10	0.000	0.000	0.014	0.301	0.204	0.315	0.218	0.219	0.154
0	15	0.000	0.000	0.015	0.315	0.217	0.330	0.232	0.230	0.164
0	20	0.000	0.000	0.016	0.336	0.235	0.352	0.251	0.246	0.178
1	0	0.002	0.000	0.051	1.222	1.596	1.275	1.649	0.885	1.134
1	5	0.002	0.000	0.053	1.221	1.601	1.276	1.656	0.886	1.140
1	10	0.003	0.000	0.056	1.218	1.618	1.277	1.677	0.890	1.156
1	15	0.003	0.000	0.062	1.215	1.641	1.279	1.706	0.895	1.179
1	20	0.003	0.000	0.069	1.204	1.674	1.276	1.746	0.897	1.211
2	0	0.080	0.000	0.119	0.000	0.448	0.200	0.647	0.235	0.534
2	5	0.082	0.000	0.123	0.000	0.437	0.205	0.641	0.242	0.533
2	10	0.087	0.000	0.131	0.000	0.407	0.219	0.626	0.258	0.530
2	15	0.096	0.000	0.145	0.001	0.360	0.243	0.601	0.286	0.525
2	20	0.110	0.000	0.162	0.007	0.299	0.279	0.571	0.325	0.520
3	0	0.931	0.000	0.205	0.533	0.942	1.670	2.078	1.516	1.788
3	5	0.946	0.000	0.211	0.528	0.946	1.685	2.103	1.534	1.813
3	10	0.984	0.000	0.227	0.513	0.957	1.724	2.168	1.582	1.878
3	15	1.049	0.000	0.251	0.489	0.970	1.789	2.271	1.660	1.981
3	20	1.142	0.000	0.282	0.452	0.986	1.877	2.411	1.766	2.122
4	0	3.199	0.008	0.291	0.436	0.065	3.933	3.562	3.730	3.483
4	5	3.212	0.008	0.300	0.440	0.070	3.959	3.589	3.756	3.510
4	10	3.245	0.008	0.323	0.450	0.084	4.026	3.660	3.826	3.582
4	15	3.291	0.010	0.359	0.465	0.109	4.125	3.769	3.930	3.693
4	20	3.344	0.011	0.405	0.483	0.148	4.243	3.908	4.054	3.830
5	0	1.567	0.100	0.358	0.067	0.185	2.092	2.210	2.081	2.160
5	5	1.532	0.102	0.369	0.071	0.178	2.075	2.181	2.067	2.138
5	10	1.439	0.108	0.399	0.081	0.158	2.028	2.105	2.029	2.081
5	15	1.287	0.119	0.445	0.098	0.129	1.950	1.981	1.965	1.985
5	20	1.086	0.135	0.507	0.123	0.092	1.851	1.820	1.882	1.862
6	0	0.723	0.549	0.395	0.018	0.544	1.685	2.211	1.593	1.944
6	5	0.750	0.556	0.408	0.016	0.538	1.730	2.252	1.640	1.988
6	10	0.821	0.575	0.443	0.011	0.522	1.850	2.361	1.763	2.103
6	15	0.938	0.605	0.496	0.006	0.495	2.045	2.534	1.962	2.288
6	20	1.101	0.647	0.568	0.001	0.454	2.317	2.770	2.238	2.540
7	0	0.873	0.944	0.401	0.152	0.522	2.369	2.740	2.096	2.343
7	5	0.844	0.941	0.414	0.147	0.524	2.346	2.723	2.081	2.332
7	10	0.766	0.931	0.450	0.136	0.528	2.284	2.676	2.042	2.303
7	15	0.642	0.913	0.507	0.118	0.533	2.181	2.596	1.975	2.252
7	20	0.480	0.880	0.584	0.095	0.535	2.040	2.480	1.887	2.180
8	0	1.181	0.101	0.378	0.256	0.290	1.917	1.950	1.867	1.890
8	5	1.198	0.094	0.392	0.253	0.296	1.937	1.979	1.895	1.923
8	10	1.242	0.074	0.427	0.244	0.310	1.988	2.054	1.965	2.009
8	15	1.303	0.048	0.484	0.230	0.333	2.064	2.168	2.071	2.140
8	20	1.361	0.020	0.560	0.207	0.363	2.148	2.303	2.194	2.297
9	0	0.005	0.433	0.337	0.274	0.094	1.049	0.870	0.926	0.806
9	5	0.008	0.440	0.350	0.273	0.099	1.071	0.897	0.949	0.833
9	10	0.022	0.456	0.382	0.270	0.111	1.130	0.972	1.014	0.909
9	15	0.058	0.478	0.435	0.263	0.132	1.234	1.103	1.129	1.042
9	20	0.133	0.498	0.508	0.253	0.162	1.392	1.302	1.305	1.244
10	0	0.610	0.036	0.286	0.232	0.009	1.164	0.942	1.141	0.993
10	5	0.586	0.031	0.297	0.233	0.011	1.147	0.925	1.130	0.983
10	10	0.523	0.019	0.326	0.234	0.016	1.102	0.884	1.102	0.956
10	15	0.421	0.006	0.373	0.236	0.025	1.036	0.825	1.060	0.919
10	20	0.289	0.000	0.438	0.236	0.042	0.962	0.768	1.015	0.886
11	0	0.899	0.360	0.233	0.170	0.005	1.662	1.496	1.520	1.410
11	5	0.900	0.357	0.242	0.172	0.004	1.671	1.503	1.533	1.421
11	10	0.898	0.348	0.267	0.176	0.002	1.689	1.514	1.560	1.444
11	15	0.879	0.328	0.307	0.182	0.000	1.696	1.514	1.586	1.465
11	20	0.823	0.289	0.362	0.189	0.002	1.664	1.476	1.586	1.461
12	0	0.394	0.099	0.182	0.113	0.033	0.788	0.708	0.760	0.706
12	5	0.412	0.106	0.189	0.115	0.031	0.823	0.738	0.792	0.736
12	10	0.459	0.126	0.209	0.120	0.024	0.914	0.818	0.880	0.816
12	15	0.529	0.159	0.241	0.127	0.015	1.057	0.945	1.017	0.942
12	20	0.611	0.201	0.287	0.136	0.006	1.235	1.105	1.189	1.102

TABLE III. Calculated widths in cm^{-1} for $^{16}O^{18}O$. [Parameters from Table I(a)].

v	N	$^5\Pi_u$	$^3\Sigma_u^+$	$^3\Pi_u$	$^1\Pi_u$	$\Gamma(F_2)$	Γ_{avg}
0	0	0.000	0.000	0.011	0.275	0.286	0.198
0	5	0.000	0.000	0.012	0.278	0.290	0.201
0	10	0.000	0.000	0.012	0.286	0.298	0.207
0	15	0.000	0.000	0.014	0.299	0.313	0.218
0	20	0.000	0.000	0.015	0.318	0.333	0.232
1	0	0.002	0.000	0.047	1.237	1.286	0.889
1	5	0.002	0.000	0.049	1.237	1.287	0.891
1	10	0.002	0.000	0.052	1.236	1.290	0.895
1	15	0.002	0.000	0.057	1.233	1.293	0.901
1	20	0.002	0.000	0.064	1.228	1.294	0.906
2	0	0.060	0.000	0.112	0.007	0.180	0.212
2	5	0.062	0.000	0.116	0.006	0.183	0.217
2	10	0.065	0.000	0.124	0.003	0.193	0.230
2	15	0.072	0.000	0.137	0.001	0.210	0.252
2	20	0.083	0.000	0.153	0.000	0.236	0.283
3	0	0.763	0.000	0.197	0.587	1.548	1.381
3	5	0.775	0.000	0.203	0.583	1.561	1.398
3	10	0.808	0.000	0.219	0.570	1.597	1.441
3	15	0.862	0.000	0.242	0.549	1.653	1.509
3	20	0.943	0.000	0.272	0.516	1.732	1.605
4	0	3.016	0.005	0.284	0.393	3.697	3.516
4	5	3.032	0.005	0.293	0.397	3.727	3.546
4	10	3.073	0.005	0.316	0.409	3.803	3.624
4	15	3.140	0.006	0.352	0.428	3.925	3.748
4	20	3.216	0.007	0.397	0.452	4.072	3.898
5	0	2.097	0.068	0.355	0.031	2.551	2.537
5	5	2.064	0.070	0.366	0.033	2.533	2.523
5	10	1.976	0.074	0.396	0.041	2.487	2.486
5	15	1.830	0.082	0.442	0.053	2.408	2.423
5	20	1.625	0.093	0.504	0.073	2.295	2.330
6	0	0.354	0.436	0.398	0.052	1.239	1.192
6	5	0.374	0.442	0.411	0.049	1.276	1.232
6	10	0.432	0.459	0.445	0.041	1.377	1.338
6	15	0.531	0.487	0.500	0.030	1.548	1.516
6	20	0.678	0.526	0.572	0.017	1.793	1.770
7	0	1.346	0.970	0.408	0.217	2.941	2.618
7	5	1.320	0.970	0.422	0.213	2.925	2.609
7	10	1.248	0.971	0.459	0.202	2.880	2.583
7	15	1.129	0.969	0.517	0.183	2.798	2.533
7	20	0.956	0.963	0.595	0.158	2.672	2.452
8	0	0.819	0.282	0.390	0.302	1.793	1.689
8	5	0.843	0.271	0.404	0.300	1.818	1.722
8	10	0.906	0.242	0.440	0.294	1.883	1.808
8	15	1.005	0.198	0.498	0.283	1.985	1.943
8	20	1.131	0.142	0.577	0.266	2.117	2.119
9	0	0.095	0.280	0.351	0.282	1.007	0.932
9	5	0.082	0.289	0.364	0.282	1.017	0.944
9	10	0.053	0.313	0.398	0.282	1.046	0.978
9	15	0.019	0.350	0.453	0.282	1.105	1.044
9	20	0.000	0.399	0.528	0.280	1.206	1.156
10	0	0.989	0.189	0.301	0.209	1.688	1.608
10	5	0.973	0.180	0.312	0.211	1.675	1.603
10	10	0.926	0.155	0.342	0.215	1.639	1.585
10	15	0.842	0.116	0.392	0.222	1.572	1.549
10	20	0.711	0.070	0.459	0.230	1.470	1.489
11	0	0.736	0.330	0.247	0.132	1.444	1.337
11	5	0.751	0.335	0.256	0.135	1.477	1.370
11	10	0.790	0.347	0.282	0.141	1.560	1.454
11	15	0.843	0.361	0.324	0.150	1.678	1.576
11	20	0.890	0.368	0.383	0.162	1.803	1.712
12	0	0.097	0.003	0.194	0.073	0.367	0.402
12	5	0.109	0.005	0.202	0.075	0.391	0.427
12	10	0.145	0.011	0.224	0.081	0.461	0.498
12	15	0.212	0.027	0.258	0.090	0.588	0.624
12	20	0.313	0.060	0.307	0.102	0.782	0.815

TABLE IV. Calculated widths in cm^{-1} for $^{18}O_2$. [Parameters from Table I(a)].

v	N	$^5\Pi_u$	$^3\Sigma_u^+$	$^3\Pi_u$	$^1\Pi_u$	$\Gamma(F_2)$	Γ_{avg}
0	0	0.000	0.000	0.010	0.260	0.270	0.187
0	5	0.000	0.000	0.010	0.263	0.273	0.189
0	10	0.000	0.000	0.011	0.270	0.281	0.195
0	15	0.000	0.000	0.012	0.283	0.295	0.205
0	20	0.000	0.000	0.013	0.300	0.314	0.218
1	0	0.001	0.000	0.044	1.249	1.293	0.891
1	5	0.001	0.000	0.045	1.249	1.295	0.894
1	10	0.001	0.000	0.048	1.250	1.299	0.899
1	15	0.001	0.000	0.053	1.250	1.304	0.905
1	20	0.002	0.000	0.059	1.249	1.309	0.912
2	0	0.044	0.000	0.105	0.023	0.173	0.198
2	5	0.045	0.000	0.109	0.021	0.174	0.201
2	10	0.048	0.000	0.116	0.016	0.180	0.211
2	15	0.052	0.000	0.129	0.009	0.190	0.227
2	20	0.060	0.000	0.144	0.003	0.207	0.251
3	0	0.608	0.000	0.189	0.638	1.434	1.255
3	5	0.617	0.000	0.194	0.634	1.446	1.270
3	10	0.644	0.000	0.209	0.624	1.477	1.308
3	15	0.688	0.000	0.232	0.607	1.527	1.369
3	20	0.754	0.000	0.261	0.580	1.595	1.453
4	0	2.763	0.003	0.276	0.338	3.380	3.227
4	5	2.781	0.003	0.285	0.343	3.412	3.259
4	10	2.828	0.003	0.308	0.356	3.495	3.343
4	15	2.906	0.003	0.342	0.377	3.628	3.477
4	20	3.004	0.004	0.387	0.405	3.800	3.650
5	0	2.628	0.044	0.351	0.007	3.030	3.005
5	5	2.600	0.045	0.362	0.008	3.015	2.995
5	10	2.525	0.048	0.392	0.011	2.976	2.967
5	15	2.399	0.053	0.438	0.019	2.909	2.917
5	20	2.213	0.061	0.498	0.032	2.804	2.834
6	0	0.081	0.328	0.399	0.106	0.914	0.899
6	5	0.092	0.333	0.412	0.102	0.939	0.927
6	10	0.123	0.346	0.447	0.092	1.009	1.006
6	15	0.183	0.370	0.502	0.076	1.131	1.141
6	20	0.283	0.403	0.574	0.056	1.316	1.340
7	0	1.754	0.927	0.415	0.287	3.382	3.033
7	5	1.738	0.931	0.429	0.283	3.380	3.036
7	10	1.691	0.940	0.467	0.273	3.371	3.041
7	15	1.607	0.953	0.527	0.255	3.341	3.038
7	20	1.471	0.969	0.605	0.231	3.276	3.008
8	0	0.381	0.523	0.401	0.332	1.637	1.468
8	5	0.403	0.511	0.415	0.331	1.661	1.499
8	10	0.461	0.481	0.453	0.329	1.724	1.583
8	15	0.560	0.432	0.513	0.323	1.828	1.721
8	20	0.702	0.363	0.594	0.314	1.972	1.911
9	0	0.467	0.103	0.365	0.264	1.199	1.177
9	5	0.444	0.110	0.379	0.265	1.198	1.178
9	10	0.383	0.130	0.414	0.270	1.197	1.184
9	15	0.291	0.164	0.471	0.276	1.202	1.199
9	20	0.181	0.215	0.549	0.281	1.226	1.235
10	0	1.160	0.397	0.316	0.164	2.036	1.899
10	5	1.160	0.388	0.328	0.166	2.042	1.911
10	10	1.156	0.365	0.360	0.173	2.053	1.939
10	15	1.136	0.325	0.411	0.184	2.056	1.969
10	20	1.084	0.268	0.483	0.198	2.032	1.986
11	0	0.355	0.172	0.261	0.081	0.869	0.855
11	5	0.374	0.180	0.272	0.084	0.910	0.894
11	10	0.427	0.201	0.299	0.090	1.017	0.999
11	15	0.512	0.236	0.344	0.101	1.193	1.171
11	20	0.627	0.282	0.406	0.116	1.430	1.403
12	0	0.013	0.064	0.208	0.031	0.316	0.353
12	5	0.009	0.058	0.216	0.033	0.316	0.357
12	10	0.002	0.042	0.239	0.037	0.320	0.373
12	15	0.003	0.021	0.276	0.045	0.346	0.415
12	20	0.030	0.004	0.329	0.057	0.420	0.507

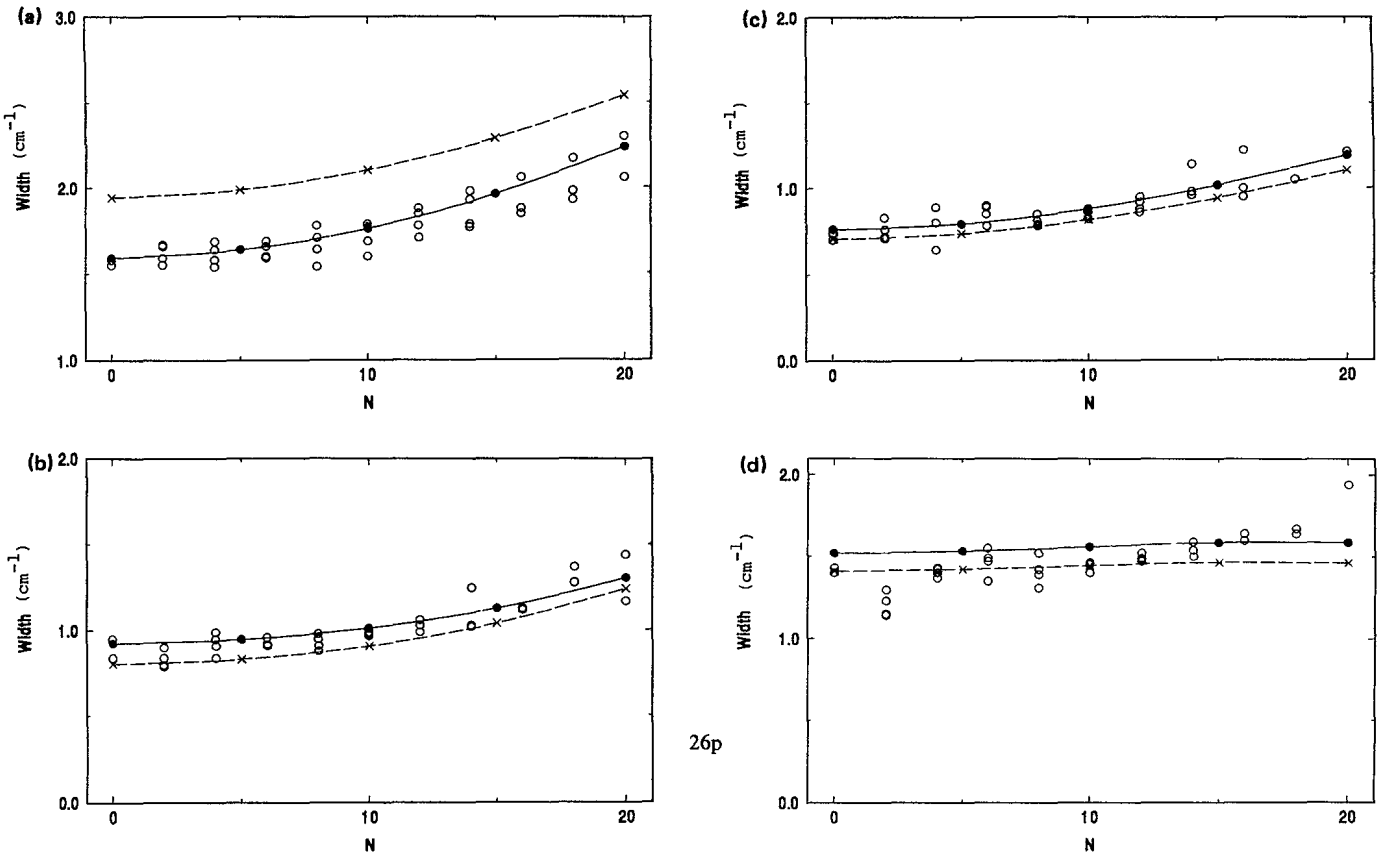

FIG. 1. The variation of the predissociation linewidth with rotational quantum number, N, shown in (a)–(d) for the $v=6$, 9, 12, and 11 of the $B\,^3\Sigma_u^-$ state of $^{16}O_2$. The average widths, Γ_{avg}, calculated using parameters in Table I(a) and I(b), are indicated respectively by the solid line with solid circles, and the broken line with crosses. The open circles indicate the experimental values of Cheung *et al.* (Ref. 15).

tory. The rotational dependence predicted for $v=1$, 3, 4, 8, and 10 is weak, in agreement with the measured widths.

Recently Cosby *et al.*[22] measured the linewidths of each fine-structure component for $v=0$ and 2 using laser-induced fluorescence spectroscopy. Their averaged linewidth for $v=2$ and $N=0$ is smaller than the value reported by Cheung *et al.*[15] Cosby *et al.*[22] suggest the discrepancy arises from the assumption of a Lorentzian line shape by Cheung *et al.* rather than the more accurate Voigt profile.

Our predicted linewidths are larger than the new measurements[22] for $v=0$ and smaller for $v=2$. The parameters in Table I(a) were inferred from experiments carried out mostly at high vibrational quantum numbers[20] and the fitting was biased towards the vibrational levels of greatest widths. The data of Cosby *et al.*[22] suggest some modification is needed of the repulsive potential energy curves and the interaction strengths.

Partridge *et al.*[23] have calculated *ab initio* potential energy curves for the $^3\Pi_u$ and $^5\Pi_u$ states. Figure 2 presents a comparison of the *ab initio* potentials with the empirical potentials constructed by Cheung *et al.*[20] The *ab initio* and empirical $^5\Pi_u$ potentials agree well in the region of their crossing with the $B\,^3\Sigma_u^-$ potential. There are small differences in the case of the $^3\Pi_u$ potential. The *ab initio* potential is consistent with the empirical crossing distance but its slope parameter M_x/V_x is 6.0 $Å^{-1}$ compared to the empirical value of 7.2 $Å^{-1}$. We have repeated the theoretical

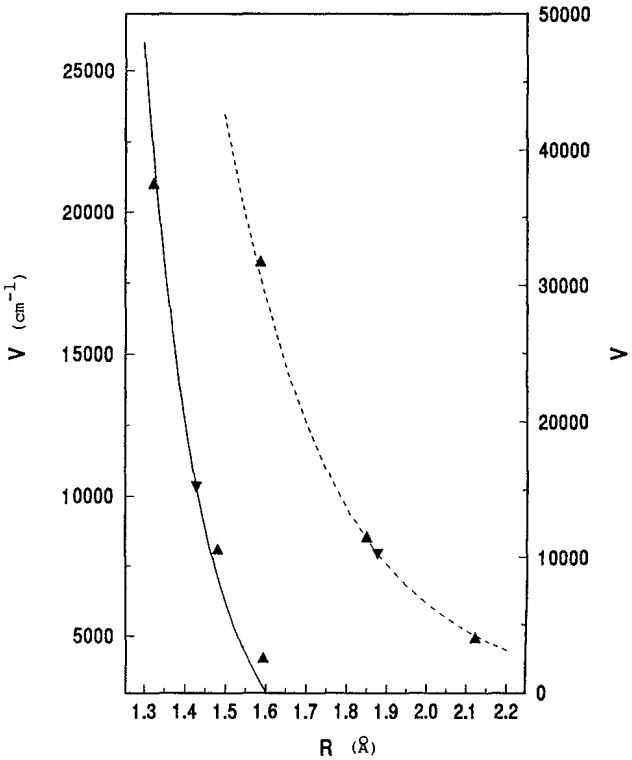

FIG. 2. Comparison of empirical and *ab initio* $^3\Pi_u$ and $^5\Pi_u$ potentials. ▼ represent the crossing points of the empirical and $B\,^3\Sigma_u^-$ potentials. ▲ represent *ab initio* values. The solid line represents the $^3\Pi_u$ potential. The broken line represents the $^5\Pi_u$ potential.

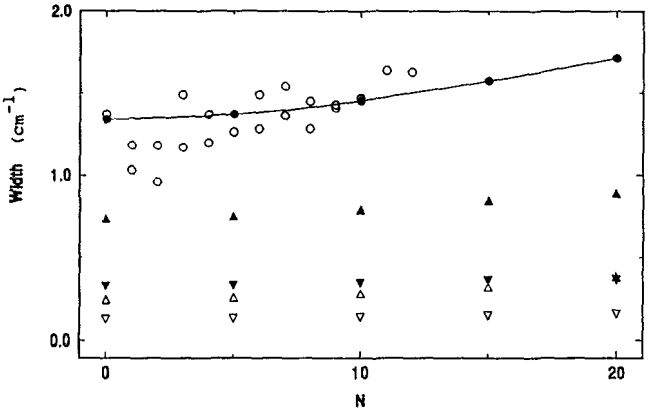

FIG. 3. The variation of the predissociation linewidth with rotational quantum number, N, of the $v=11$ level of the $B\,^3\Sigma_u^-$ state of $^{16}O^{18}O$. The calculated average widths, Γ_{avg}, are indicated by the solid line and solid circles, with open circles for the experimental values of Chiu *et al.* (Ref. 17). ▲, ▼, △, ▽ represent the contributions to the calculated total F_2 width from the interactions between $B\,^3\Sigma_u^-$ and $^5\Pi_u$, $^3\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$, respectively.

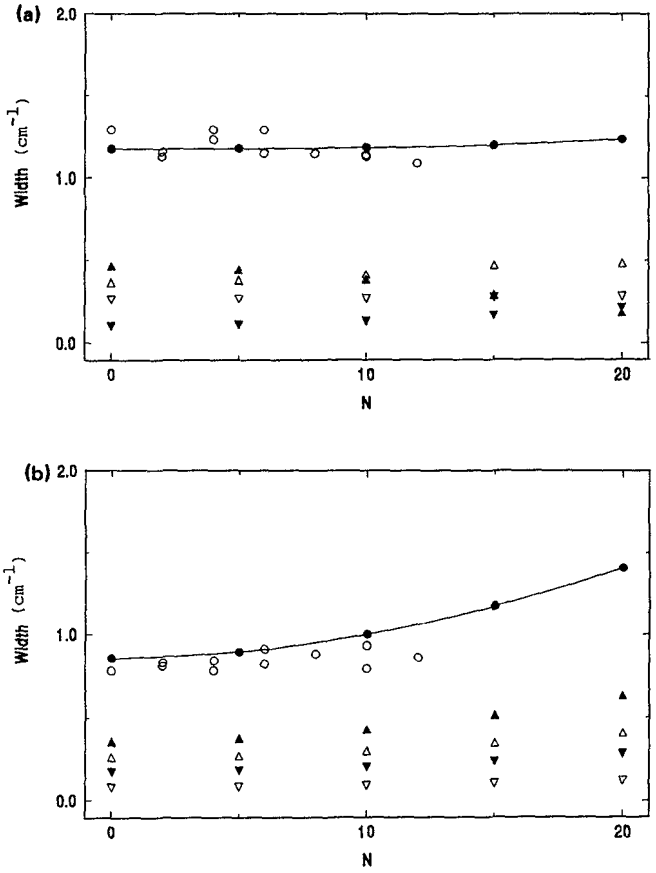

FIG. 4. The variation of the predissociation linewidth with rotational quantum number, N, shown in (a)–(b) for $v=9$ and 11 of the $B\,^3\Sigma_u^-$ state of $^{18}O_2$. The calculated average widths, Γ_{avg}, are indicated by the solid line and solid circles, with open circles for the experimental values of Chiu *et al.* (Ref. 17). ▲, ▼, △, ▽ represent the contributions to the calculated total F_2 width from the interactions between $B\,^3\Sigma_u^-$ and $^5\Pi_u$, $^3\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$, respectively.

calculations with the *ab initio* potential but there is little change in the predicted widths and the discrepancies are not resolved. It appears necessary to modify the $^1\Pi_u$ potential. The contributions from the interaction of the $B\,^3\Sigma_u^-$ and $^1\Pi_u$ states for $v=2$ are very sensitive to the details of the potential energy curves. We present in Table I(b) an alternative set of parameters for the $^1\Pi_u$ state and in Table II the resulting linewidths. The averaged widths are included in Figs. 1(a)–1(d). The agreement between theory and experiment for $v=0$ and 2 is greatly improved, though the dependence on N is not accurately reproduced, but the modified potential parameters of Table I(b) yield poorer agreement with the $v=6$ and $v=7$ widths, as Fig. 1(a) and Table II demonstrate.

We have used the parameters in Table I(a) to predict linewidths for the $^{16}O^{18}O$ and $^{18}O_2$ isotopes. Chiu *et al.*[17] have reported tentatively a rotational dependence up to $N=14$ in the $v=3$ and 11 levels of $^{16}O^{18}O$ and the $v=3$, 9 and 11 levels of $^{18}O_2$. Figures 3 and 4 compared the theoretical and experimental averaged linewidths. The agreement with the limited data is satisfactory.

The empirical potentials of Chiu *et al.*[20] provide a plausible account of the overall pattern of the linewidths as functions of v and N and the calculations confirm the importance at high values of N of the l-uncoupling interaction of the $B\,^3\Sigma_u^-$ and $^3\Pi_u$ states, noted by Julienne,[4] Yang *et al.*,[18] and Cosby *et al.*[22] The ratio η/ξ, characterizing the relative strengths of the l-uncoupling and spin–orbit interactions of the $^3\Pi_u$ state, that we obtain from the data of Chiu *et al.*[17] is 0.03. The value agrees with that derived by Cosby *et al.*[22] The absolute strengths of the empirical interactions are larger than those calculated *ab initio* by Julienne.[24] The strength of the interaction with the $^1\Pi_u$ state is twice that given by Cosby *et al.*[22] and there remain significant discrepancies between theory and measurement for specific values of N and v. More data on low-lying vibrational levels of the $^{16}O^{18}O$ and $^{18}O_2$ isotopes would help in resolving the discrepancies. Reliable calculations of the potential energy curves of the $^1\Pi_u$ and $^3\Sigma_u^+$ states, complementing those of Partridge *et al.*[23] on the $^3\Pi_u$ and $^5\Pi_u$ states would be of particular value.

ACKNOWLEDGMENTS

We thank Dr. P. C. Cosby and Dr. T. G. Slanger for providing us with a preprint prior to publication. A. S-C. C. thanks the Smithsonian Institution for International Exchange Scholarships and the Physical Science Research Fund of the University of Hong Kong for financial support and D. K-W. M. thanks the Croucher Foundation for his Studentship. The work of A. D. and M. J. J. was partly supported by the National Science Foundation, Division of Atmospheric Sciences under Grant No. ATM-9019188. M. F. was a visitor to the Harvard–Smithsonian Institute for Theoretical Atomic and Molecular Physics. This work reported was also supported by NASA Upper Atmospheric Research Program under Grant No. NAG5-484 to the Smithsonian Astrophysical Observatory.

[1] P. Krupenie, J. Phys. Chem. Ref. Data **1**, 423 (1971).
[2] J. N. Murrell and J. M. Taylor, Mol. Phys. **6**, 609 (1969).
[3] M. S. Child, J. Mol. Spectrosc. **33**, 487 (1970).

[4] P. S. Julienne and M. Krauss, J. Mol. Spectrosc. **56**, 270 (1975).
[5] P. S. Julienne, J. Mol. Spectrosc. **63**, 60 (1976).
[6] M. L. Sink and A. D. Bandrauk, J. Chem. Phys. **66**, 5313 (1977).
[7] B. R. Lewis, J. H. Carver, T. I. Hobbs, D. G. McCoy, and H. P. F. Gies, J. Quant. Spectrosc. Radiat. Transfer **20**, 191 (1978).
[8] J. E. Frederick and R. D. Hudson, J. Mol. Spectrosc. **74**, 247 (1979).
[9] B. R. Lewis, J. H. Carver, T. I. Hobbs, D. G. McCoy, and H. P. F. Gies, J. Quant. Spectrosc. Radiat. Transfer **22**, 213 (1979).
[10] H. P. F. Gies, S. T. Gibson, D. G. McCoy, A. J. Blake, and B. R. Lewis, J. Quant. Spectrosc. Radiat. Transfer **26**, 469 (1981).
[11] B. R. Lewis, L. Berzins, J. H. Carver, and S. T. Gibson, J. Quant. Spectrosc. Radiat. Transfer **36**, 187 (1986).
[12] B. R. Lewis, L. Berzins, and J. H. Carver, J. Quant. Spectrosc. Radiat. Transfer **37**, 229 (1987).
[13] B. R. Lewis, L. Berzins, and J. H. Carver, J. Quant. Spectrosc. Radiat. Transfer **37**, 243 (1987).
[14] A. S-C. Cheung, K. Yoshino, D. E. Freeman, R. S. Friedman, A. Dalgarno, and W. H. Parkinson, J. Mol. Spectrosc. **134**, 362 (1989).
[15] A. S-C. Cheung, K. Yoshino, J. R. Esmond, S. S-L. Chiu, D. E. Freeman, and W. H. Parkinson, J. Chem. Phys. **92**, 842 (1990).
[16] D. E. Freeman, A. S-C. Cheung, K. Yoshino, and W. H. Parkinson, J. Chem. Phys. **91**, 6538 (1990).
[17] S. S-L. Chiu, A. S-C. Cheung, K. Yoshino, J. R. Esmond, D. E. Freeman, and W. H. Parkinson, J. Chem. Phys. **93**, 5539 (1990).
[18] X. Yang, A. M. Wodtke, and L. Hüwel, J. Chem. Phys. **94**, 2469 (1991).
[19] H. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, New York, 1986).
[20] S. S-L. Chiu, A. S-C. Cheung, M. Finch, M. J. Jamieson, K. Yoshino, A. Dalgarno, and W. H. Parkinson, J. Chem. Phys. **97**, 1787 (1992).
[21] R. S. Friedman, J. Quant. Spectrosc. Radiat. Transfer **43**, 225 (1990).
[22] P. C. Cosby, H. Park, Richard A. Copeland, and T. G. Slanger, J. Chem. Phys. **98**, 5117 (1993).
[23] H. Partridge, C. W. Bauschlicher, Jr., S. R. Langhoff, and P. R. Taylor, J. Chem. Phys. **95**, 8292 (1991).
[24] P. S. Julienne (private communication, 1991).