

Predicted predissociation linewidths in the Schumann–Runge bands of O₂ compared with recent high resolution measurements

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We derive and use new parameters to quantify the semiempirical expressions of Julienne and Krauss [J. Mol. Spectrosc. **56**, 270 (1975)] for the $^5\Pi_u$, $^3\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$ potentials that predissociate the rovibrational levels of the $B^3\Sigma_u^-$ state of O₂. Using the new parameters in the model of Julienne and Krauss we evaluate fine-structure predissociation linewidths for the Schumann–Runge bands that terminate on the $v=13,14$ rovibrational levels of the $B^3\Sigma_u^-$ state. We compare these linewidths and those calculated with several existing sets of parameters with the measurements of Dooley *et al.* [J. Chem. Phys. **109**, 3856 (1998)]. We also show the deperturbing effect of the level shifts, calculated with the new parameters, on the energies of the rotationless $v=0-17$ vibrational levels of the $B^3\Sigma_u^-$ state. © 2001 American Institute of Physics. [DOI: 10.1063/1.1361255]

I. INTRODUCTION

The Schumann–Runge bands of O₂ exhibit triplets that reflect the fine-structure components, F_1 , F_2 , and F_3 , of the rovibrational levels supported by the ground electronic state, $X^3\Sigma_g^-$, and the upper electronic state, $B^3\Sigma_u^-$. However, the fine-structure components are not easily extracted from observed spectra because the fine-structure splittings of the $B^3\Sigma_u^-$ and the $X^3\Sigma_g^-$ levels and many of the predissociation linewidths are close in size.¹ Cheung *et al.*² obtained predissociation linewidths for vibrational levels $v=0-12$ of the $B^3\Sigma_u^-$ state from photoabsorption cross section measurements of Yoshino *et al.*³⁻⁵ They did not distinguish between the fine-structure components and obtained averaged linewidths.

Differences in the fine-structure components were found in laser induced fluorescence experiments by Wodtke *et al.*⁶ for vibrational levels $v=14-16$ of the $B^3\Sigma_u^-$ state. Few precision measurements of rotationally dependent fine-structure specific linewidths are available. Existing measurements include those obtained in laser induced fluorescence experiments by Yang *et al.*⁷ for a few high rotational states of the vibrational levels $v=10,11$ and by Cosby *et al.*⁸ for many rotational states of the vibrational levels $v=0,2$. By analyzing photoabsorption cross sections measured by Yoshino *et al.* at room temperature,⁹ Lewis *et al.*¹ have provided more data; they inferred fine-structure specific linewidths for various rotational states of the vibrational levels $v=1,2,5,7,9-13$. Recently, Dooley *et al.*¹⁰ have made very precise width measurements by three different techniques (UV laser spectroscopy, laser induced fluorescence spectroscopy and vacuum-ultraviolet Fourier-transform spectroscopy), which agree well with each other, for many rotational levels for $v=13,14$.

Parameters defining the semiempirical potentials and in-

teractions in the predissociation model of Julienne and Krauss¹¹ have been obtained by least squares fitting techniques by Cheung *et al.*¹² for averaged rotationally dependent linewidths for the isotopomers $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$, and by Lewis *et al.*¹ for the fine-structure linewidths found by them from the ($^{16}\text{O}_2$) data of Yoshino *et al.*⁹ With the increasing availability of fine-structure resolved data there is a need for further exploration of the prediction of predissociation linewidths.

Cheung *et al.*¹² determined the parameters by fitting data for vibrational levels $v=0-12$. In this investigation we have modified the parameters by including, in the fitted data, the fine-structure data of Cosby *et al.*⁸ for vibrational levels $v=0,2$ and of Lewis *et al.*¹ for vibrational levels $v=1,2,9-12$; we used neither the data of Yang *et al.*⁷ nor the data of Lewis *et al.* for vibrational levels $v=5,7$ because they contain comparatively little rotational information. We made the new fit to the same range of vibrational levels used by Cheung *et al.*¹² ($v=0-12$). Then we used the new data of Dooley *et al.*¹⁰ as a sensitive test of our choice of parameters by comparing the predicted linewidths with these measurements. Finally, we calculated the level shifts and studied their deperturbing effect on the rotationless $v=0-17$ vibrational energies.

II. THE CALCULATIONS

A. Widths

We calculated the widths according to the model of Julienne and Krauss¹¹ as did Lewis *et al.*¹ The method is as follows.

The equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_B(R) + \frac{\hbar^2}{2\mu R^2} J(J+1) - E \right] \chi_{vJ}(R) = 0 \quad (1)$$

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is solved where μ is the reduced mass of the molecule, R is the nuclear separation and $R^{-1}\chi_{vJ}(R)$ is the normalized radial wave function for the bound rovibrational state (v, J) with energy E supported by the $B^3\Sigma_u^-$ potential $V_B(R)$ and, for each predissociated electronic state, the equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_C(R) + \frac{\hbar^2}{2\mu R^2} J(J+1) - E \right] \chi_{kJ}(R) = 0 \quad (2)$$

is solved where $R^{-1}\chi_{kJ}(R)$ is the radial continuum wave function with wave number $k = (1/\hbar) \times \sqrt{2\mu[E + V_B(\infty) - V_C(\infty)]}$ (asymptotic) in the predissociating potential $V_C(R)$, normalized so that its amplitude is $\sqrt{2/\pi k}$ at infinite separation. Numerical methods are necessary to solve Eqs. (1) and (2). With these solutions the matrix elements

$$\xi = \int_0^\infty dR \chi_{vJ}(R) V_{so}(R) \chi_{kJ}(R) \quad (3)$$

are evaluated where $V_{so}(R)$ is the spin-orbit interaction between the $B^3\Sigma_u^-$ bound state and the predissociated state. The fine-structure widths are determined from the formulas in Table I in which the additional Coriolis (or l uncoupling) interaction between the $B^3\Sigma_u^-$ bound state and the $^3\Pi_u$ predissociated state^{7,11,13} is accounted for by the parts of the formulas that depend on the ratio $\rho = \eta/\xi$ where η is the coupling constant defined by Yang *et al.*;⁷ the uncoupling parameters, a and b , are given by

$$a = a(v, J) = \sqrt{\frac{F_2(v, J) - F_1(v, J)}{F_3(v, J) - F_1(v, J)}} \quad (4)$$

$$b = b(v, J) = \sqrt{\frac{F_3(v, J) - F_2(v, J)}{F_3(v, J) - F_1(v, J)}} \quad (5)$$

where $F_1(v, J)$, $F_2(v, J)$, and $F_3(v, J)$ are the energies of the three fine-structure components for level (v, J) . The expressions given for these energies by Miller and Townes^{14,15} imply that

$$a(v, J) = \sqrt{\frac{1}{2} + \frac{\lambda - \left(B - \frac{\gamma}{2}\right)}{2 \sqrt{\left[\lambda - \left(B - \frac{\gamma}{2}\right)\right]^2 + 4J(J+1)\left(B - \frac{\gamma}{2}\right)^2}}} \quad (6)$$

and

$$b(v, J) = \sqrt{\frac{1}{2} - \frac{\lambda - \left(B - \frac{\gamma}{2}\right)}{2 \sqrt{\left[\lambda - \left(B - \frac{\gamma}{2}\right)\right]^2 + 4J(J+1)\left(B - \frac{\gamma}{2}\right)^2}}} \quad (7)$$

where B denotes the rotational constant and λ and γ denote other constants for vibrational level v . In our calculations we used the values of B , λ , and γ that were fitted to experimental data by Cheung *et al.*¹⁶

This procedure yields widths for a given value of the total angular momentum quantum number J . The experimental data are reported in terms of the quantum number N of the angular momentum of the end over end rotation. For electronic Σ states these angular momenta differ only by the spin angular momentum of the pair of unmatched electrons and N is related to J for each fine-structure component as indicated in Table I. The fine-structure specific widths are clearly seen to differ.

B. Shifts

In the current and previous work¹⁷ we used the Green's function method described by Du *et al.*¹⁸ to obtain the shifts at the band heads where $J=0$. Lewis *et al.*¹ found the shifts differently. For each predissociating electronic state and a range of energies E they solved the coupled equations, to which Eqs. (1) and (2) are approximations for $J=0$,

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_B(R) - E \right] \chi'_v(R) = V_{so}(R) \chi'_k(R) \quad (8)$$

and

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_C(R) - E \right] \chi'_k(R) = V_{so}(R) \chi'_v(R), \quad (9)$$

where $R^{-1}\chi'_v(R)$ and $R^{-1}\chi'_k(R)$ are radial wave functions; they found the shifted energies by seeking resonances in the phase shifts of $\chi'_k(R)$ and determined the shifts by subtracting the corresponding eigenenergies, for $J=0$, of Eq. (1). The Green's function method that we used is simpler in that it requires no search of phase shifts but it does require the solution of an inhomogeneous differential equation.

C. Potentials and interactions

We used the empirical $B^3\Sigma_u^-$ RKR potential of Friedman.¹⁹ Molecules in the $^5\Pi_u$, $^3\Sigma_u^+$, $^3\Pi_u$, and $^1\Pi_u$ electronic states dissociate by separating two O(3P) atoms; the interaction between these molecular states and the $B^3\Sigma_u^-$ state predissociates the bound levels of the $B^3\Sigma_u^-$ state. For these predissociating state potentials we used the expression of Julienne and Krauss,¹¹

$$V(R) = V_x \exp[-(M_x/V_x)(R - R_x)], \quad (10)$$

with various sets of values of the parameters V_x and M_x , which are the values and slopes of each potential where it crosses the $B^3\Sigma_u^-$ potential, and R_x , which is the location of each crossing; each potential is referred to its asymptotic value at infinite atomic separation.

We used the representation of Julienne and Krauss¹¹ for the spin-orbit interaction of each predissociated state with the $B^3\Sigma_u^-$ state:

$$V_{so}(R) = A_x \exp[-a(R - R_x)^2] \quad (11)$$

($a = 1 \text{ bohr}^{-2}$), where A_x is a parameter. We represented the additional Coriolis interaction by the ratio ρ defined in Sec. II A; its contribution to the widths is shown in Table I.

TABLE I. Fine-structure widths Γ in the Julienne and Krauss model.

State	$\frac{\Gamma(F_1)}{2\pi\xi^2}$	$\frac{\Gamma(F_2)}{2\pi\xi^2}$	$\frac{\Gamma(F_3)}{2\pi\xi^2}$
$^5\Pi_u$	$1 + \frac{b^2}{6}$	$\frac{7}{6}$	$1 + \frac{a^2}{6}$
$^3\Sigma_u^+$	b^2	1	a^2
$^3\Pi_u$	$1 + a^2 + 2[J(J+1)-1]\rho^2 - 4\sqrt{2}ab\rho\sqrt{J(J+1)}$	$1 + 2J(J+1)\rho^2 + 2\sqrt{2}\rho$	$1 + b^2 + 2[J(J+1)-1]\rho^2 + 4\sqrt{2}ab\rho\sqrt{J(J+1)}$
$^1\Pi_u$	b^2	1	a^2
	$N=J-1$	$N=J$	$N=J+1$

D. Least squares fit

It is implied in Sec. IIC that we have at our disposal three parameters A_x , R_x , and M_x for each predissociating potential and the parameter ρ . The parameter V_x is not disposable because it is the value of the $B^3\Sigma_u^-$ state potential at separation R_x . The parameter ρ is not disposable *within the hypothesis of pure precession*¹³ but would be determined by the $B^3\Sigma_u^-$ and $^3\Pi_u$ state potentials because the parameter η of Yang *et al.*⁷ (see Sec. IIA) would be given by¹²

$$\eta = \int_0^\infty dR \chi_{vJ}(R) \frac{1}{2\mu R^2} \chi_{kJ}(R). \quad (12)$$

Equation (12) shows that η depends on the vibrational quantum number v . However, the integrals (3) and (12) are almost proportional to the overlap integral $\int_0^\infty dR \chi_{vJ}(R) \chi_{kJ}(R)$ and hence, within the hypothesis of pure precession, the ratio ρ is independent of the vibrational quantum number.¹² We assume that independence holds when ρ is evaluated as a disposable parameter; i.e., we do not need a separate value for each vibrational quantum number. Comparison of the value obtained for ρ as a disposable parameter with the value calculated from Eqs. (3) and (12) indicates the departure from pure precession.

The parameters were adjusted as follows. We started with the set of parameters given in Table I(a) of Ref. 12 by Cheung *et al.* and modified them incrementally in an attempt to account for the fine-structure specific data for the rotational states of the vibrational levels $v=0-2,9-12$ discussed in Sec. I. Since the contributions of the $^5\Pi_u$ and the $^3\Sigma_u^+$ states to the predissociation linewidths of the $B^3\Sigma_u^-$ state for $v \leq 2$ are negligibly small, but the contributions of the $^3\Pi_u$ and $^1\Pi_u$ states are significant, it was necessary to adjust the parameters of the $^3\Pi_u$ and $^1\Pi_u$ states. For each trial set of parameters we predicted the fine-structure specific linewidths according to the model of Julienne and Krauss as described in Secs. IIA and IIC. We calculated the standard deviation of the predicted widths from the data for the $v=0-2,9-12$ vibrational levels and adjusted the parameters to minimize this quantity.²⁰

III. RESULTS AND DISCUSSION

We show the new values of the parameters and also, for comparison, the values found in other work, in Table II.

A. Widths

In Figs. 1–7 we compare the new calculated widths with the data to which they were fitted. The agreement is good but we note some deviations; first, the F_1 components are a little small for $v=0$, $N \leq 12$ and for $v=10$ and all N shown; second, the F_2 components are too small for $v=0$, $N \leq 16$ and for $v=1$ and 10 and all N shown; third, the F_3 component is too small for $v=10$ and, finally, all three components fit the data of Lewis *et al.*¹ better than that of Cosby *et al.*⁸ for $v=2$.

In Figs. 8–13 we compare the widths predicted by the new parameters and by the others listed in Table II, with the

TABLE II. Parameters for interactions with the $B^3\Sigma_u^-$ state.

State	$^5\Pi_u$	$^3\Sigma_u^+$	$^3\Pi_u$	$^1\Pi_u$
	New values			
A_x (cm ⁻¹)	70	46	35	28
R_x (Å)	1.879	1.999	1.454	1.724
M_x (cm ⁻¹ Å ⁻¹)	38 650	49 000	64 000	22 700
ρ			0.024	
	Values given by Cheung <i>et al.</i> in Table I(a) of Ref. 12			
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
ρ			0.029	
	Values of Lewis <i>et al.</i> (Ref. 1)			
A_x (cm ⁻¹)	69.9	29.7	30.8	28.3
R_x (Å)	1.8787	2.009	1.454	1.724
M_x (cm ⁻¹ Å ⁻¹)	41 000	27 600	55 600	23 000
ρ			0.0189	
	Ab initio values (Refs. 1 and 11)			
A_x (cm ⁻¹)	65	45	28	25
R_x (Å)	1.880	2.004	1.457	1.724
M_x (cm ⁻¹ Å ⁻¹)	41 900	40 800	58 700	23 000
ρ			0.018	

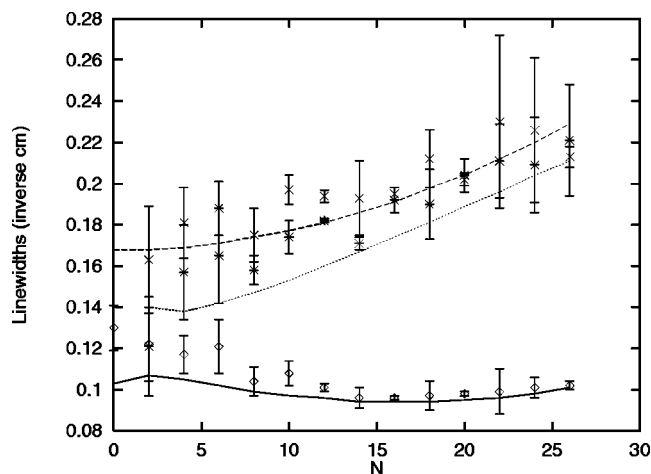


FIG. 1. Linewidths for $v=0$. Calculated: this work F_1 full line, F_2 dashed line, F_3 dotted line. Experiment: Cosby *et al.* (Ref. 8) F_1 \diamond , F_2 \times , F_3 $*$.

experimental results of Dooley *et al.*¹⁰ for $v=13,14$; the tabulated measurements were obtained by vacuum-ultraviolet laser spectroscopy (VUVLS) and laser-induced fluorescence spectroscopy (LIFS). It is seen that, except for the F_1 and F_3 components with $v=14$, the predictions from the new parameters represent the best overall fit to the experimental data although the widths of the F_1 and F_3 components with $v=13$ predicted from the parameters of Lewis *et al.*¹ are better for the higher values of N . Our calculated F_1 linewidths for the levels with $v=13$ and $N<14$ agree well with the experimental measurements; however, at $N=14$ the calculated and experimental values begin to differ.

The fits to experiment of the F_1 linewidths with $v=14$ obtained with the *ab initio*^{1,11} and the Lewis parameters are good for the values of N shown, the better fit being that obtained from the Lewis values; although the N dependence of these linewidths obtained from the new parameters is qualitatively correct in having the expected “S” shape, the fit to experiment is not satisfactory. Previous calculations^{1,12,17} and the present work suggest that there is considerable sensitivity to the fitted data. To allow these dis-

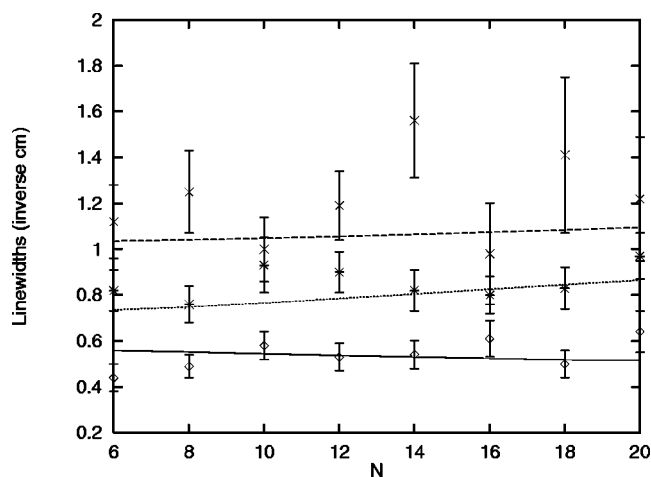


FIG. 2. Linewidths for $v=1$. Calculated: this work F_1 full line, F_2 dashed line, F_3 dotted line. Experiment: Lewis *et al.* (Ref. 1) F_1 \diamond , F_2 \times , F_3 $*$.

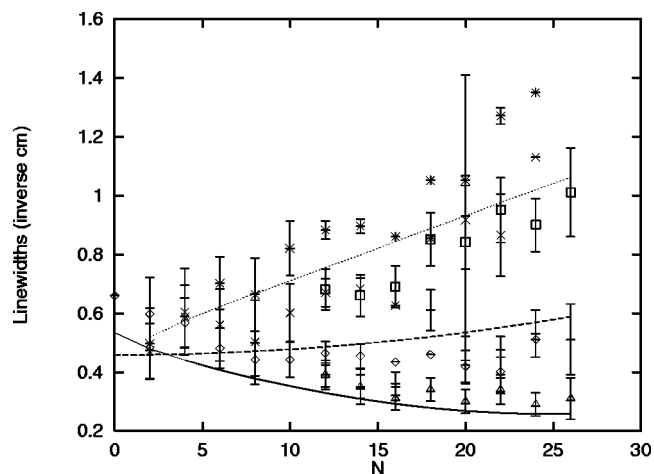


FIG. 3. Linewidths for $v=2$. Calculated: this work F_1 full line, F_2 dashed line, F_3 dotted line. Experiment: Cosby *et al.* (Ref. 8) F_1 \diamond , F_2 \times , F_3 $*$, Lewis *et al.* (Ref. 1) F_1 \triangle , F_2 $-$, F_3 \square .

crepancies in the F_1 linewidths to be investigated properly any uncertainties in the calculated values that reflect uncertainties in the fitted data must be eliminated. New measurements of the $v=0-12$ fine-structure data, made with precision comparable to that achieved by Dooley *et al.*,¹⁰ are needed in such a study. The fits of the F_3 linewidths with $v=14$ obtained with the new parameters and with the *ab initio* parameters are also only satisfactory but the fit obtained from the Lewis parameters is good. In all cases the parameters of Cheung *et al.*¹² yield widths which are too large and, except for the F_1 and F_3 components with $v=14$, the *ab initio* parameters yield widths which are too small.

Cheung *et al.*¹² calculated the value of ρ as 0.029 within the hypothesis of pure precession; they used the value of ξ obtained by Chiu *et al.*¹⁷ in their analysis, for $J=0$, of measurements on the isotopomers $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$, and $^{18}\text{O}_2$. We would obtain the same value for ρ if we assumed pure precession because the new parameters for the $^3\Pi_u$ potential are the same as those used by Cheung *et al.*¹² and Chiu *et al.*;¹⁷ the new value of 0.024 differs from the value above, reflecting the departure from pure precession. Lewis *et al.*¹ ob-

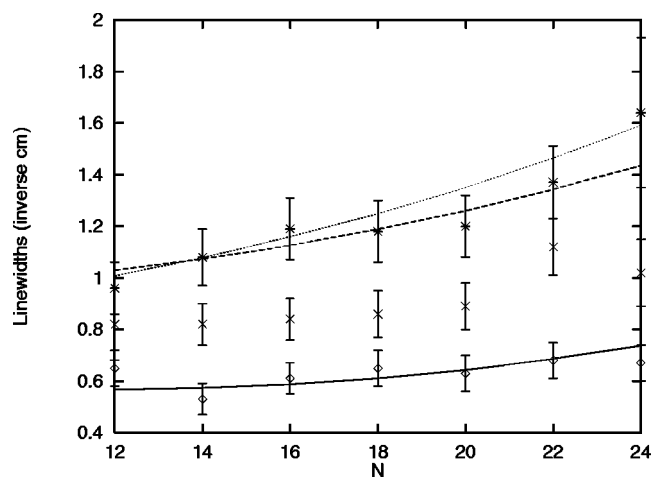


FIG. 4. Linewidths for $v=9$. Calculated: this work F_1 full line, F_2 dashed line, F_3 dotted line. Experiment: Lewis *et al.* (Ref. 1) F_1 \diamond , F_2 \times , F_3 $*$.

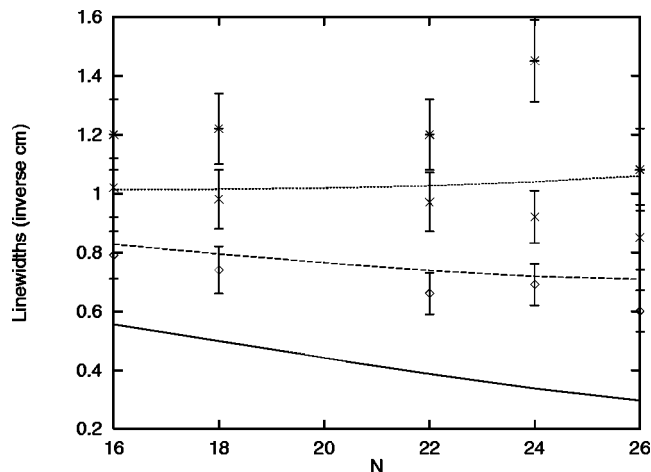


FIG. 5. Linewidths for $v=10$. Calculated: this work F_1 full line, F_2 dashed line, F_3 dotted line. Experiment: Lewis *et al.* (Ref. 1) F_1 \diamond , F_2 \times , F_3 $*$.

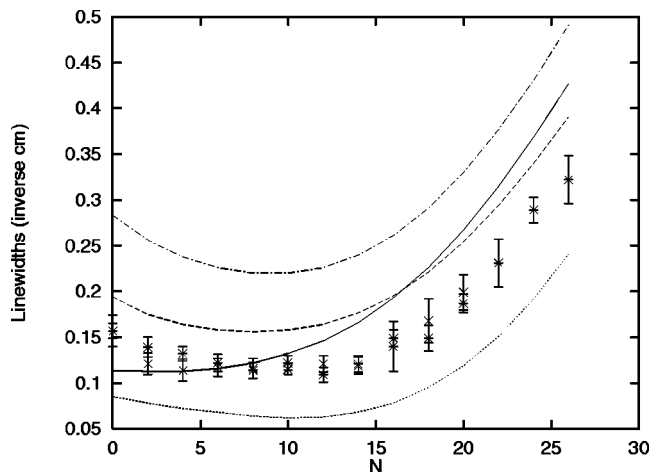


FIG. 8. F_1 linewidths for $v=13$. Calculated: this work full line, Lewis *et al.*¹ dashed line, *ab initio* Lewis *et al.* (Ref. 1) and Julienne and Krauss (Ref. 11) dotted line, Cheung *et al.* (Ref. 12) dotted/dashed line. Experiment: Dooley *et al.* (Ref. 10) VUVLS \times , LIFS $*$.

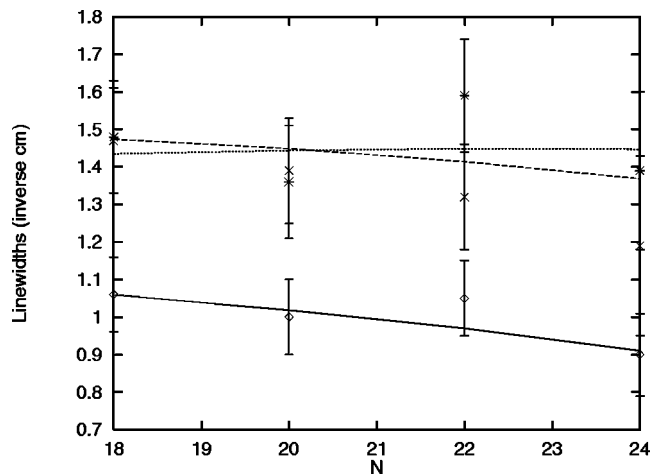


FIG. 6. Linewidths for $v=11$. Calculated: this work F_1 full line, F_2 dashed line, F_3 dotted line. Experiment: Lewis *et al.* (Ref. 1) F_1 \diamond , F_2 \times , F_3 $*$.

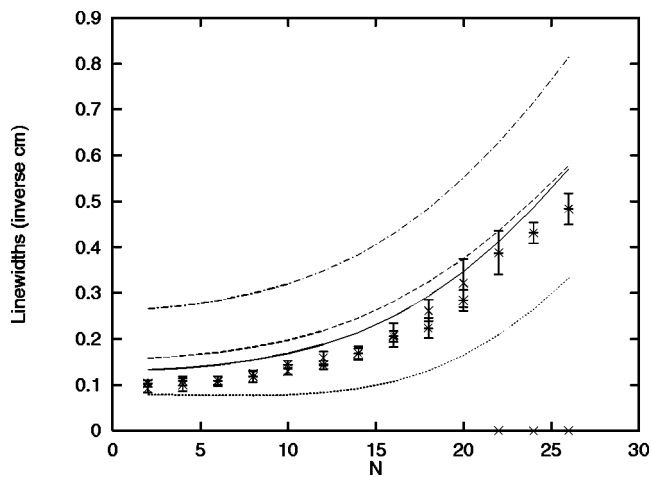


FIG. 9. F_2 linewidths for $v=13$. Calculated: this work full line, Lewis *et al.* (Ref. 1) dashed line, *ab initio* Lewis *et al.* (Ref. 1) and Julienne and Krauss¹¹ dotted line, Cheung *et al.* (Ref. 12) dotted/dashed line. Experiment: Dooley *et al.* (Ref. 10) VUVLS \times , LIFS $*$.

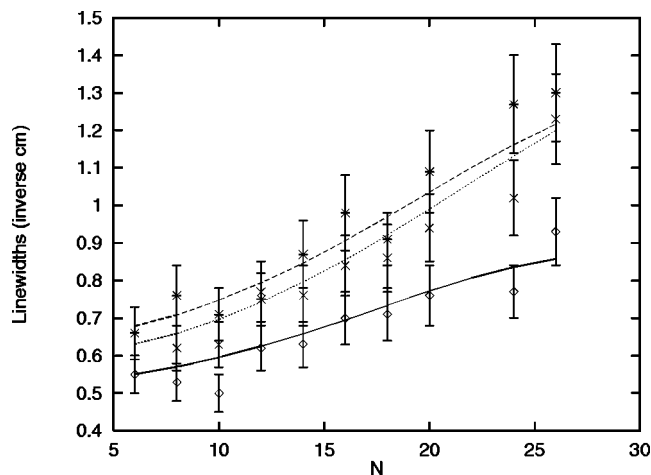


FIG. 7. Linewidths for $v=12$. Calculated: this work F_1 full line, F_2 dashed line, F_3 dotted line. Experiment: Lewis *et al.* (Ref. 1) F_1 \diamond , F_2 \times , F_3 $*$.

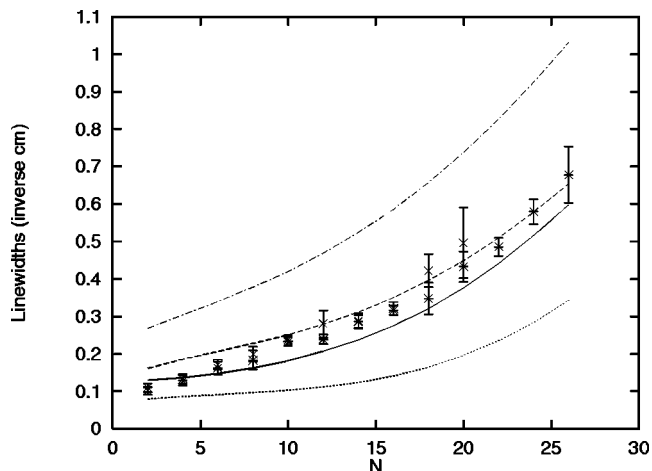


FIG. 10. F_3 linewidths for $v=13$. Calculated: this work full line, Lewis *et al.* (Ref. 1) dashed line, *ab initio* Lewis *et al.* (Ref. 1) and Julienne and Krauss (Ref. 11) dotted line, Cheung *et al.* (Ref. 12) dotted/dashed line. Experiment: Dooley *et al.* (Ref. 10) VUVLS \times , LIFS $*$.

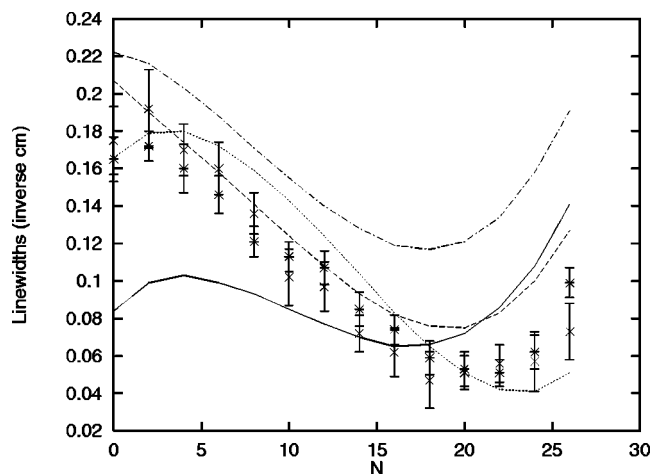


FIG. 11. F_1 linewidths for $v=14$. Calculated: this work full line, Lewis *et al.* (Ref. 1) dashed line, *ab initio* Lewis *et al.* (Ref. 1) and Julienne and Krauss (Ref. 11) dotted line, Cheung *et al.* (Ref. 12) dotted/dashed line. Experiment: Dooley *et al.* (Ref. 10) VUVLS \times , LIFS $*$.

tained the smaller value of 0.0189. Having noted that the difference between the F_3 and F_1 component widths of the $^3\Pi_u$ state is proportional to the product $\xi\eta$ or $\xi^2\rho$ for large values of J or N they suggested that ρ can be determined independently of the least squares fit once ξ is known. We note, from Table I, that by forming the ratio of the difference to the sum of the F_3 and F_1 component widths we obtain an expression in ρ which is independent of ξ ;

$$\frac{\Gamma(F_3) - \Gamma(F_1)}{\Gamma(F_3) + \Gamma(F_1)} = \frac{b^2 - a^2 + 8\sqrt{2}ab\rho\sqrt{J(J+1)}}{3 + 4[J(J+1) - 1]\rho^2}. \quad (13)$$

We solved the quadratic equation (13) in ρ and obtained estimates corresponding to the measurements of Dooley *et al.*,¹⁰ in each case choosing the smaller root because it has the expected linear dependence on the width ratio when the product $J\rho$ is small. We averaged over the rovibrational states with $v=13,14$ and obtained $\rho=0.024$ from the LIFS measurements and $\rho=0.019$ from the VUVLS measure-

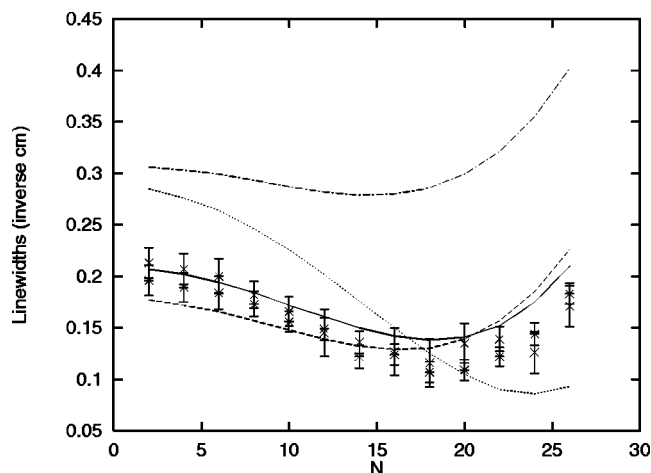


FIG. 12. F_2 linewidths for $v=14$. Calculated: this work full line, Lewis *et al.* (Ref. 1) dashed line, *ab initio* Lewis *et al.* (Ref. 1) and Julienne and Krauss (Ref. 11) dotted line, Cheung *et al.* (Ref. 12) dotted/dashed line. Experiment: Dooley *et al.* (Ref. 10) VUVLS \times , LIFS $*$.

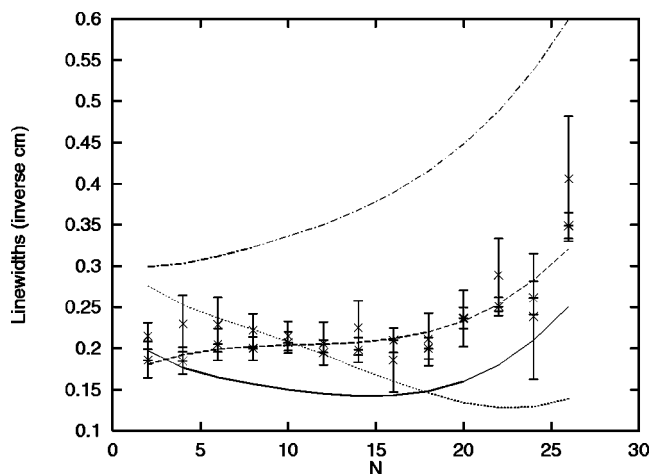


FIG. 13. F_3 linewidths for $v=14$. Calculated: this work full line, Lewis *et al.* (Ref. 1) dashed line, *ab initio* Lewis *et al.* (Ref. 1) and Julienne and Krauss (Ref. 11) dotted line, Cheung *et al.* (Ref. 12) dotted/dashed line. Experiment: Dooley *et al.* (Ref. 10) VUVLS \times , LIFS $*$.

ments; the new value and that of Lewis *et al.*¹ seem to be equally plausible and further experimental study of the widths induced by the Coriolis interaction between the $B^3\Sigma_u^-$ and the $^3\Pi_u$ states is needed to provide evidence for determining which value is the most appropriate.

B. Shifts

The effects of the predissociating interactions on the energies of the rovibrational states supported by the $B^3\Sigma_u^-$ potential are magnified in the second vibrational differences;¹¹ the second difference is

$$\Delta^2 F_2(v) = F_2(v+1,0) - 2F_2(v,0) + F_2(v-1,0) \quad (14)$$

for the F_2 vibrational level v with $J=0$ (and therefore $N=0$). We calculated the shifts that are induced by the predissociating interactions for $v=0-17$. The level shift contribution to the second vibrational difference is given by

$$\Delta^2 S(v) = S(v+1) - 2S(v) + S(v-1), \quad (15)$$

where $S(v)$ is the shift in the F_2 energy of the vibrational level with vibrational quantum number v with $J=0$. The *deperturbed* second difference

$$\Delta^2 F_2^0(v) = \Delta^2 F_2(v) - \Delta^2 S(v) \quad (16)$$

is expected to show smoother dependence on v than does the second difference in Eq. (14).^{11,13} The second differences are negative because the spacing of the levels in the $B^3\Sigma_u^-$ potential decreases as v increases and the contributions from the level shifts in Eq. (15) are small; we show the second differences in Fig. 14 with the signs reversed. Figure 14 demonstrates the smoothing effect of the shifts, calculated with the new parameters, on the energies given by Cheung *et al.*;¹⁶ the differences are centered on vibrational levels $v=1-16$.

IV. CONCLUSION

In conclusion we have obtained a new set of parameters to describe the potentials and interactions responsible for

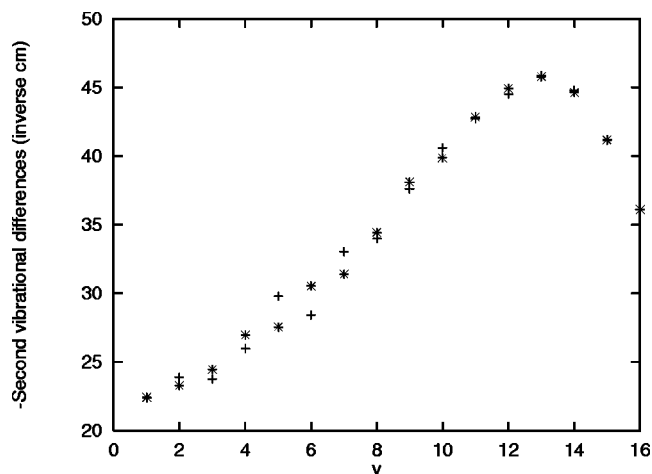


FIG. 14. Second vibrational differences. Calculated: this work *. Experiment: Cheung *et al.* (Ref. 16) +.

predissociating the levels supported by the $B^3\Sigma_u^-$ potential. The agreement between measured widths and the widths obtained when our parameters are used in the model of Julienne and Krauss¹¹ is good for the F_1 , F_2 , and F_3 fine-structure levels of the $v=13$ vibrational state and for the F_2 fine-structure level of the $v=14$ vibrational state, but is not satisfactory for the F_1 and F_3 fine-structure levels of the $v=14$ vibrational state. The new parameters yield an approximately smooth dependence of the deperturbed second order rotationless energy on vibrational quantum number. Agreement with experiment is better in some cases when predicted with the parameters of Lewis *et al.*¹ and better in some cases when predicted with our new values; either set provides a plausible account of the predissociation of the rovibrational levels of the $B^3\Sigma_u^-$ state. The branching ratio for the products $O(^3P)+O(^3P)$ and $O(^3P)+O(^1D)$ has been measured by Lin *et al.*²¹ but its value does not lead to a sensitive distinction between the sets of parameters; for example the calculations of Balakrishnan *et al.*²² show good agreement with experiment when either of the sets of parameters given by Cheung *et al.* in Tables I(a) and I(b) of Ref. 12 is used. The new parameters and those of Lewis *et al.*¹ depend largely on linewidths that were obtained from photoabsorption cross sections. As the determination of these fine-structure linewidths is probably close to the limit of information that can be ex-

tracted from the photoabsorption measurements, experimental data for $v=0-12$ of as high quality as that of Dooley *et al.*¹⁰ would be very valuable in a further search for a better set of parameters.

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