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Isotopic dependence of predissociation linewidths in the Schumann-Runge bands of oxygen

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Recent work on predissociation in the Schumann-Runge (B 3Σ+ u−X 3Σ− u) system of oxygen encourages a study of the isotopic dependence of the linewidths. It has been shown that the predissociation is dominated by the spin-orbit coupling to the repulsive 5Πu state with smaller contributions from couplings to the 3Πu, 1Πu, and 3Σ+ u states. Additionally the orbit-rotation interaction between the B 3Σ+ u and 3Πu states has been demonstrated to be important for lines emanating from high rotational states. In this Note we describe the isotopic dependence of the linewidths.

In Mulliken’s classification of predissociation the crossing of the potential energy curves of the 3Πu and B 3Σ+ u states is of type C− (where the predissociating state crosses the repulsive branch of the bound state) and crossings of the 5Πu, 1Πu, and 3Σ+ u states are of type C+. The predissociating states cross the attractive branch. Within the semiclassical approximation the width Γν, caused by one of the predissociating states, of the vibrational level with quantum number ν and energy Eν (measured from the bottom of the well) satisfies

\[ \frac{\Gamma_{ν}}{\hbar \omega_{ν}} = πC(\frac{3}{2} \phi_{ν})^{2/3} (E_{ν} − E_{x})^{−1/2} A_{ν} [−(\frac{7}{2} \phi_{ν})^{2/3}], \]

where \( \hbar \omega_{ν} = dE_{ν}/dv \) and C are given in Ref. 9, \( \phi_{ν} \) is a phase (given in Ref. 9 for a C− crossing and in Ref. 10 for a C+ crossing), \( E_{x} \) is the energy at the crossing point and \( A_{ν} \) denotes the Airy function. We have previously described the calculation of the predissociation linewidths for oxygen based on a least squares fit to experimental data.4 Letting \( \mu \) denote the ratio of the reduced mass for any one of the three oxygen isotopomers \( ^{16}O_{2} \), \( ^{16}O^{18}O \) and \( ^{18}O_{2} \) to that of the reference isotopomer \( ^{16}O_{2} \) we see, from Ref. 9, that the phases \( \phi_{ν} \) and the quantity C scale as \( \mu^{-1/2} \). Hence the characteristic energy \( E∗^{ν} \) in the (linear) approximation,

\[ \left( \frac{3}{2} \phi_{ν} \right)^{2/3} ≈ \left( E_{ν} − E_{x} \right)^{−1/2} A_{ν} \frac{(E_{ν} − E_{x})}{E∗^{ν}}, \]

scales as \( \mu^{-1/3} \). Within this approximation we can determine the dependence of the width on the energy \( E_{ν} \). This dependence may be expressed as

\[ \frac{\Gamma_{ν}}{\hbar \omega_{ν}} = K \mu^{2/3} A_{ν} \left[ −\mu^{1/2}(E_{ν} − E_{x}) \right], \]

where \( K \) is mass independent and \( E∗^{ν} \) is the value of \( E^{ν} \) for the reference isotopomer \( ^{16}O_{2} \). Expression (1) goes over smoothly to sinusoidal variation for \( E ≫ E_{x} \). Within approximation (2) this becomes

\[ \frac{\Gamma_{ν}}{\hbar \omega_{ν}} = K\left(\frac{E_{x}}{E∗^{ν}}\right)^{1/2} \mu^{1/2}(E_{ν} − E_{x})^{−1/2} \sin^{2} \left( \frac{\mu^{1/2} \phi_{ν} + \pi}{4} \right), \]

where \( \phi_{ν} \) is the phase for the reference isotopomer \( ^{16}O_{2} \).

Equations (3) and (4) show that the widths depend in a complicated manner on the reduced mass and do not have the simple dependence we implied. Figure 2 of Ref. 4 could be viewed to imply that the widths can be fitted to a universal curve for all isotopomers. However this conclusion is ambiguous because the points are fortuitously distributed so as to obscure the mass dependence. Furthermore Fig. 2 of Ref. 4 shows the total widths; more precise information is obtained from the individual linewidths. We illustrate this briefly with a sample of calculated widths for two predissociating states: the 3Πu of type C− where the Airy fit (3) is appropriate and the 5Πu where the sine fit (4) is appropriate.

Figure 1 shows the 3Πu widths for each isotopomer. It is clear that all three sets of widths do not fit a universal curve. This was obscured in the plot in Ref. 4 of the total widths. The energies were calculated from equation (5) below.

Our 3Πu widths are in the sinusoidal region where equation (4) is appropriate. Because of the disposition of points it is not so obvious from a direct fit that each isotopomer fits a unique curve. However equation (4) clearly shows a mass dependence. To show that the linear approximation, which leads to equation (4), is appropriate for our 3Πu calculations we have calculated the corresponding phases and we show, in Fig. 2, that the quantity \( (\frac{3}{2} \phi_{ν})^{2/3} \mu^{-1/3} \) plotted as a function of energy \( E_{ν} \), has the linear form of equation (2). The energies were calculated from Ref. 11

\[ E_{ν} = (v + 1/2) \omega_{ν} \mu^{-1/2} − (v + 1/2)^2 \omega_{ν} x_{ν} \mu^{-1} + (v + 1/2)^3 \omega_{ν} y_{ν} \mu^{-3/2}, \]

where \( \omega_{ν} \) was taken as 709.31 cm−1, \( \omega_{ν} x_{ν} \) as 10.65 cm−1 and \( \omega_{ν} y_{ν} \) as −0.139 cm−1. The dependence of \( E_{ν} \) on \( \mu \), being dominated by the first term on the right hand side of equation (5), can be largely removed by simple scaling. Equation (5) also provides \( \hbar \omega_{ν} = dE_{ν}/dv \). The values of

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FIG. 1. Width (cm$^{-1}$) vs energy (cm$^{-1}$) in predissociation by the $^3\Pi_u$ state.

FIG. 2. $(\frac{3}{5} \phi_\nu)^{\nu^3/\mu} - 10$ vs energy (cm$^{-1}$) in predissociation by the $^5\Pi_u$ state.
$E^\ast_0 = 573 \text{ cm}^{-1}$, $E_x = 2550 \text{ cm}^{-1}$ and $K = 4.481$ were calculated by the method described in Ref. 10. The graph of the dimensionless quantities $(\frac{2}{5} \phi_e)^{2/5} \mu^{-1/5}$ and the intercept $(E_x,0)$ vs energies is expected to be a line with slope $1/E^\ast_0$. Figure 2 demonstrates this; from the slope we find the value of $E^\ast_0$ to be $557 \text{ cm}^{-1}$ compared with $573 \text{ cm}^{-1}$ given above. The $v = 11$ vibrational level of $^{16}\text{O}_2$ and the $v = 10$ vibrational level of $^{18}\text{O}_2$ are off line. This occurs because in each of these cases the phase is $\pi/4$ greater than a multiple of $\pi$ causing its evaluation from the width to be ill conditioned.

In conclusion we see that in semiclassical theory, in contrast to the vibrational energy levels, the dependence of the predissociation widths on the reduced mass cannot be removed by a simple scaling procedure. We have shown this for previously calculated widths and we have resolved an ambiguity.

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