

Comments on the changes made to the program July 18, 2007

I made an error associated with parity in the original program. It appears to affect very low J values, but is averaged out for systems with high J. Here is the origin of the problem. Equation (A2) from the paper is

$$I(\theta, \nu) = C \sum_{J'', M'', P'', F''} \text{Pop}(J'', M'', F'') \times \left| \sum_{J'=J''-1}^{J''+1} \left\{ \sum_{M', P', F', \Omega'', \Omega'} \alpha''_{\Omega''} \alpha'_{\Omega'} L(\nu, J'', F'', J', F') \right\} \times A(J'', M'', \Omega'', \Omega', J') \right|^2 \times \left\{ N(J') \sum_{\Omega'} \alpha'_{\Omega'} d_{M', \Omega'}^{J'}(\theta) \right\}$$

Within that absolute value squared are two sums. The first has to do with the intensities of transitions (the spectrum depends on this) and it is a weighting factor for the calculation of beta. The second is the wavefunction for the dissociative state; while not explicit in the notation it depends on parity through the  $\alpha'$  functions. The equation is correct except that each of the terms in this second sum should be multiplied by an *electronic* wavefunction corresponding to the case (a) basis set, i.e., each should be multiplied by  $|\Omega'\rangle$ . The correct version of (A2) should then read

$$I(\theta, \nu) = C \sum_{J'', M'', P'', F''} \text{Pop}(J'', M'', F'') \times \left| \sum_{J'=J''-1}^{J''+1} \left\{ \sum_{M', P', F', \Omega'', \Omega'} \alpha''_{\Omega''} \alpha'_{\Omega'} L(\nu, J'', F'', J', F') \right\} \times A(J'', M'', \Omega'', \Omega', J') \right|^2 \times \left\{ N(J') \sum_{\Omega'} \alpha'_{\Omega'} d_{M', \Omega'}^{J'}(\theta) |\Omega'\rangle \right\}$$

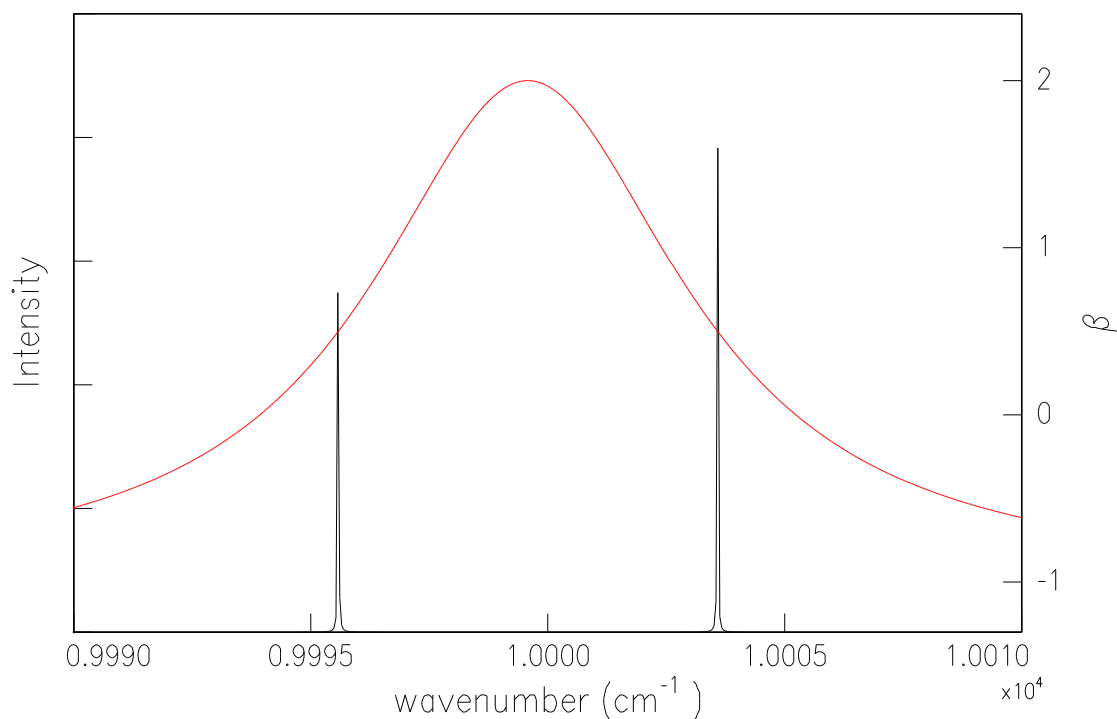
Note that since these  $|\Omega'\rangle$  electronic functions are orthogonal, when the second term is multiplied by its complex conjugate all the cross terms (of different  $\Omega'$ ) will vanish. In the original formula (and in the program) these cross terms were mistakenly kept.

The solution taken in the program is to recognize ahead that these cross terms vanish and to replace the above formula with the equivalent form given below:

$$I(\theta, \nu) = C \sum_{J'', M'', P'', F''} \text{Pop}(J'', M'', F'') \times \sum_{\Omega'} \left| \sum_{J'=J''-1}^{J''+1} \left\{ \sum_{M', P', F', \Omega'', \Omega'} \alpha''_{\Omega''} \alpha'_{\Omega'} L(\nu, J'', F'', J', F') \right\} \times A(J'', M'', \Omega'', \Omega', J') \right|^2 \times \{ N(J') \alpha'_{\Omega'} d_{M', \Omega'}^{J'}(\theta) \}$$

Note that the sum over  $\Omega'$  has been moved outside the absolute value signs. About four lines of code were changed in each of the subroutines Coherent.f and CohHiJ.f, as noted in the comments. Unfortunately, the program runs a bit slower as a result of this change.

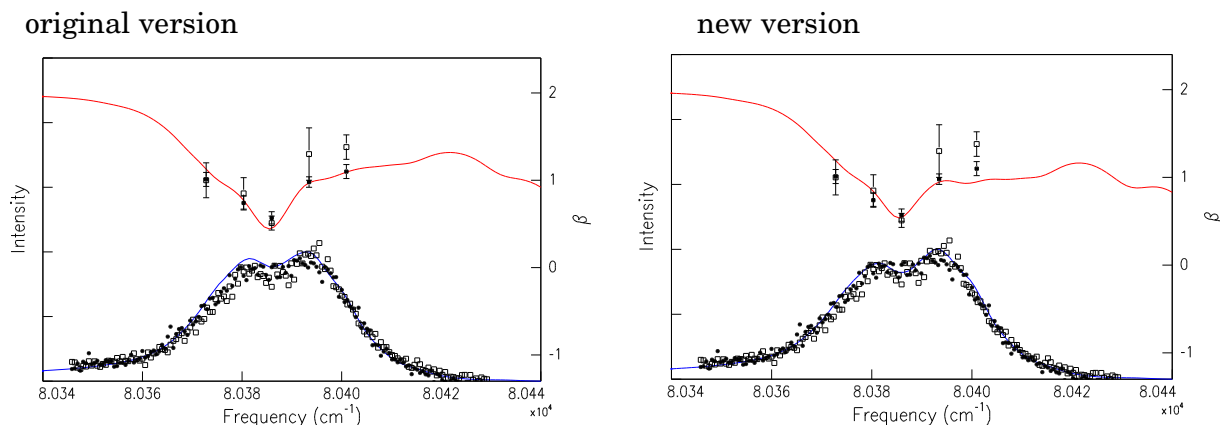
The important effect of this change is that the program agrees with the recent result of Vladislav V. Kuznetsov and Oleg S. Vasyutinskii (JCP, to be published), where in Appendix A they show that  $\beta$  for a singlet sigma to singlet pi transition on the Q(1) line should be 0.5, in contrast to the prediction of  $\beta = -1$  by Liyanage and Gordon. Here are some representative results showing the Q(1) and P(1) lines for such a transition in the limit of very slow dissociation:



I am grateful to Oleg Vasutinski and Greg Hall for pointing out this error.

I have checked to see if this error affects other calculations that we have performed. The new versions of Figures 7 and 8 of our paper is indistinguishable from the published ones.

Figure 10 is slightly different, but not appreciably:



Thus, it does not appear that any of the major conclusions of the original paper are changed by the error that has now been corrected.

A note on centrifugal distortion.

It's included in the original program for singlet states.

I believe that it can be added simply for doublets and triplets, but I have not checked the results. Here's how I would start (these are the changes to the fortran):

line 437 of ain.f, subtract  $Dx * ((J+.5)*(J+1.5))^{**2}$

line 442 of ain.f, subtract  $Dx * ((J-.5)*(J+.5))^{**2}$

the above two changes correct doublets

line 473 of ain.f, subtract  $Dx * (J*(J+1.))^{**2}$

lines 478 and 481, ditto

the above three changes correct triplets