Supplementary Material (ESI) for PCCP

Supplementary information

for

Duschinsky Mixing between Four Non-totally Symmetric Normal Coordinates in the S_1–S_0 Vibronic Structure of Phenylvinylacetylene: A Quantitative Analysis

Christian W. Müller[a,*], Josh J. Newby[a], Ching-Ping Liu[b], Chirantha P. Rodrigo[a], Timothy S. Zwier[a]

[a] Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907-2084
[b] Institute of Chemistry, Academia Sinica, Taipei, 11529 Taiwan

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A note on intensity discrepancies in the simulated SVLF spectra and the ambiguity concerning the identity of S_0 level 48_4

To correct for the intense scattered light perturbing the resonance fluorescence intensities of the SVLF spectra, a 300 s scattered light acquisition was subtracted from a 300 s fluorescence acquisition for each spectrum. It is obvious from Figures 3 and 4, however, that this correction was not sufficient to systematically remove all scattered light from the resonance transitions. Nonetheless, it should be noted that it is a consistent feature of our simulations that in the deviating cases (Figure 4) the experimental resonance fluorescence intensities are greater than the simulated intensities, thus indicating incomplete subtraction of scattered light.

Besides the discrepancies concerning the intensities of the resonance transitions, the simulated intensities of only two (out of 434) vibrational transitions differ strongly enough from their experimental counterparts to deserve special mention: the $47_1^2 48_3^0$ transition at 231 cm^{-1} in the 47^2 SVLF spectrum and the $46_0^2 48_4^0$ transition at 201 cm^{-1} in the 46^2 SVLF spectrum. Both have simulated intensities approximately six times the corresponding experimental intensities. The discrepancy in the former case seems to be unsystematic since the corresponding transitions to the $47_1 48_3$ level in all other cold SVLF spectra do not show similarly large differences. The discrepancy in the latter case is singular in the same sense. However, it affects a transition to the 48_4 level which has been noted in section 4 and in the Note Added in Proof to Paper I to suffer from an ambiguity. Based on the simulation of the S_0 torsional potential of mode ν_{48} carried out in Paper I, we assigned the band at 186 cm^{-1} in the 0^0 SVLF spectrum to the 48_4^0 transition. This assignment afforded the best agreement in the least-squares sense between the experimental

and the simulated torsional frequency spacings (Table 6 of Paper I). Moreover, it implies only moderate anharmonicity for the S_0 torsional potential as assessed by comparison between the frequency of the 48_4 level ($186\,cm^{-1}$) and the frequency of the only other observed overtone 48_2 ($89\,cm^{-1}$). In contrast, an alternative possibility for the assignment of level 48_4 was found based on intensity evidence instead of frequency spacings. This alternative is the band at $201\,cm^{-1}$ (see Table 1). It afforded the best agreement in the least-squares sense between the experimental intensities of the corresponding transitions to level 48_4 in our cold SVLF spectra and the simulated intensities obtained from the Duschinsky fit. It has to be noted, however, that the Duschinsky fit with the 48_4 frequency set to $186\,cm^{-1}$ instead of $201\,cm^{-1}$ yielded parameters nearly identical to those in Table 3. Consequently, the simulated spectra resulting from this fit strongly resemble those given in Figures 3 and 4 except that the intensities at $201\,cm^{-1}$ are shifted to $186\,cm^{-1}$. Due to this discrepancy between intensity and frequency spacing evidence and due to the fact that the alternative torsional potential simulation with 48_4 set to $201\,cm^{-1}$ and the alternative Duschinsky fit with 48_4 set to $186\,cm^{-1}$ equally deteriorate to a small, but noticeable degree, this ambiguity concerning the identity of the 48_4 level has to remain unresolved. It is, however, of minuscule importance to the overall Duschinsky analysis as well as to the S_0 torsional potential simulation of Paper I.