ANALYSIS OF THE VISIBLE ABSORPTION SPECTRUM OF I_2 IN INERT SOLVENTS USING A PHYSICAL MODEL

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Absorption spectra of I_2 dissolved in n-heptane and CCl_4 are analyzed with a quantum gas-phase model, in which spectra at four temperatures between 15C and 50C are least-squares fitted by bound-free spectral simulations to obtain estimates of the excited-state potential energy curves and transition moment functions for the three component bands: $A - X$, $B - X$, and $C - X$. Compared with a phenomenological band-fitting model used previously on these spectra, the physical model (1) is better statistically, and (2) yields component bands with less variability. The results support the earlier tentative conclusion that most of the 20 percent gain in intensity in solution is attributable to the $C - X$ transition. The T-dependent changes in the spectrum are accounted for by potential energy shifts that are linear in T and negative (giving red shifts in the spectra) and about twice as large for CCl_4 as for heptane. The derived upper potentials resemble those in the gas phase, with one major exception: In the statistically best convergence mode, the A potential is much lower and steeper, with a strongly varying transition moment function. This observation leads to the realization that two markedly different potential curves can give nearly identical absorption spectra.