ANOMALOUS ROTATION-TRANSLATION COUPLING EFFECTS IN CARBON MONOXIDE ISOTOPOMERS TRAPPED IN SOLID PARAHYDROGEN

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Crystal Field (CF) theory, which assumes that the center of mass (C.M.) of a dopant molecule remains fixed at the center of a rigid trapping cage, cannot explain simultaneously the effective rotational constants and M_J dependent splittings observed for CO molecules isolated in solid parahydrogen (pH_2). Rotation-Translation Coupling (RTC) theory,[a] which permits motion of the molecular C.M., and the Pseudorotating Cage (PC) model,[b] which allows for dynamic deformations of the trapping cage, seem likely candidates for improvement over CF theory. A key concept in RTC theory is the "center-of-interaction" (C.I.) which is loosely defined as the point within the dopant molecule about which the anisotropy of environmental interactions is minimized. For heteronuclear diatomic dopants the C.I. may be different from the C.M.; at equilibrium in a rigid trapping cage, the C.I. will coincide with the cage center. To first order, all pure RTC models predict perturbations to rotational energies that depend quadratically on the separation between the C.I. and the C.M., denoted here as å. Isotopic substitution in CO permits the systematic manipulation of the location of the C.M. Analysis of the rovibrational absorption spectra of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{13}C^{18}O$ in solid pH_2 reveals an excellent linear correlation between B_{eff}/B and å. Extrapolation of these lines back to B_{eff}/B = unity, i.e. vanishing matrix perturbations to the rotational spacings, predicts a C.I. location 0.25(0.01)Åcloser to the C atom than the C.M. of the $^{12}C^{16}O$ isotopomer, in excellent agreement with estimates based on an ab-initio CO-H_2 intermolecular potential.[c] Unfortunately, the existing PC model makes no explicit prediction of the dependence of rotational energies on cage deformations in terms of the parameter å; further theoretical work along these lines is required.

[a] H. Friedmann and S. Kimel, J. Chem. Phys. v43, p3925 (1965).
[b] J. Manz, J. Am. Chem. Soc. v102, p1801 (1980).
[c] P. Jankowski and K. Szalewicz, to be published.