Ar MATRIX TRAPPING SITES FOR CYCLOBUTADIENE

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The possibility of quantum mechanical tunneling by cyclobutadiene (CB) remains of interest, and the present MO computations relating to Ar matrix trapping sites of CB were motivated by the spectral observations of Michl et al. Their IR and ^{13}CMR spectra[a,b] suggest that automerization occurs at a rate faster than 10^3 s^{-1} in the Ar-isolated CB system, while they found only one transition, rather than a widely spaced doublet, for the automerization mode in the Raman[c,d] spectrum. The present MO computations consider CB:Ar$_n$ clusters based on ccp and hcp Ar lattice fragments at the MP2/6-311++(2d,2p) level of MO theory. The results suggest: a) the feasibility for energy offsets of the asymmetrical double-minimum PES of CB that are greater than 35 cm^{-1} in some Ar trapping sites - i. e. larger than needed to depopulate[c,d] the upper Raman doublet component; and b) that the global PES for the Ar/CB matrix system can achieve symmetrical double-minimum character when modest trapping site rearrangement accompanies the CB automerization. The observation of what may be very slow tunneling by Ar-isolated CB in comparison with estimated free molecule rates is then explainable in terms of the adiabatically separated fast CB automerization mode and slow trapping site adjustment.

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