SPECTROSCOPY AND RELAXATION KINETICS OF MATRIX ISOLATED CH/D RADICALS

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We have investigated the properties of matrix isolated CD and present a comparison with earlier studies of the CH radical. The CH/D radicals were formed by the microwave dissociation of methane. The products were trapped in solid Ar or Kr at 12 K and investigated using laser excitation and dispersed fluorescence techniques. The $B^2\Sigma^-$-$X^2\Pi$ and $A^2\Delta$-$X^2\Pi$ transitions were studied. The decay of CH(B) v = 0 is primarily radiative in both Ar and Kr with small contributions from B→A nonradiative transfer. Fluorescence was not detected from CD(B), v = 0, as the B→A transfer process was much faster than radiative decay for this isotope. Differences in the B→A energy gaps are responsible for the large difference in the transfer rates of the two isotopes.

Excitation spectra yield evidence that CH/D(B) rotates in solid Ar and Kr matrices. Low frequency structure in the B-X (0,0) absorption band changed considerably on H/D isotopic substitution while it was relatively insensitive to the replacement of the matrix material. Absorption spectra for the A-X transition did not show evidence for rotation in the matrix, but it is likely that optical selection rules prevent the observation of rotational structure in this instance.

Vibrational relaxation of CH/D(B) is faster for the heavier isotope, indicating that vibration to rotation energy transfer is the dominant relaxation mechanism.

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