ELECTRONIC SPECTROSCOPY AND RELAXATION DYNAMICS OF MATRIX ISOLATED CH

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We have reexamined the properties of matrix isolated CH[a] for comparison with recent studies of the CH-Ar van der Waals complex[b,c]. As in previous work[a], CH radicals were formed by microwave dissociation of methane. The products were trapped in solid Ar or Kr at 12 K, and probed using laser excitation and dispersed fluorescence techniques. Excitation of the $B^2\Sigma^- - X^2\Pi$ system yielded fluorescence from the v'= 0 and 1 vibrational levels. The lifetime for v'= 0 was consistent with radiative relaxation, while the v'= 1 lifetime was shortened by vibrational relaxation ($k_v \approx 7x10^5\ s^{-1}$ in both Ar and Kr). The B-X bands showed zero-phonon leading edges with blue-shaded phonon wings. Sub-structure in the phonon wings was consistent with excitation of the CH-Ar stretch mode.

The A-X absorption bands were similar in appearance to the B-X features. Fluorescence from the A state could be excited at energies well above the zero-phonon transitions. Previously it was thought that B-A transfer was not involved in this process. However, in the present study we find evidence for a small contribution from B-A transfer. The B-X and A-X transitions exhibit red-shifts on trapping in Ar or Kr. This is typical behavior, but it is surprising when data for the CH-Ar binary complex are considered. The gas-phase complex shows blue-shifted origins for both the B-X and A-X transitions. Increasing the size of the clusters moves the absorption bands to even higher energies. Attempts to reconcile the cluster and matrix behavior, using models based on additive pair-wise interactions, will be presented.

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