

ARGON PRE-DISSOCIATION INFRARED SPECTROSCOPY OF TRAPPED INTERMEDIATES IN THE $O^- + CH_4 \rightarrow OH^- + CH_3$ REACTION

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We characterize trapped reaction intermediates in the $O^- + CH_4 \rightarrow OH^- + CH_3$ ion-molecule reaction using argon predissociation spectroscopy in the 2400 to 3800 wavenumber range. This reaction is calculated to display a classic double-minimum potential surface, and the trapped complex observed here is assigned to the exit channel, OH-CH₃, ion-radical isomer. This assignment is based on the observation of a sharp, strong band at 3590 wavenumbers. This band displays a progression in the bare complex, which is interpreted with the aid of ab initio calculations. Vibrational motion on this surface is calculated to be quite floppy, and the progression is due to high amplitude motion arising from a barely frustrated rotation about the H- bond to the ion.