Abstract

Electronic-to-vibrational (E-V) energy transfer is a significant kinetic channel in the collisional quenching of spin-orbit excited chlorine atoms, Cl\(^*\) (\(^2\)P\(_{1/2}\), 882 cm\(^{-1}\)), by molecular collision partners. In the present study Cl\(^*\) atoms are prepared in the presence of CH\(_4\) or CD\(_4\), under pseudo first-order conditions, by photolysis of ICl at 532 nm with a pulsed Nd:YAG laser. Quenching of Cl\(^*\) by CH\(_4\) or CD\(_4\) results in E-V excitation of the \(v_4\) asymmetric bending mode as observed by infrared (IR) fluorescence from the vibrationally excited products. Time-resolved IR fluorescence observations of CH\(_4\)(\(v_4\)) and CD\(_4\)(\(v_4\)) are consistent with a simple kinetic scheme involving direct E-V excitation of CH\(_4\)(\(v_4\)) or CD\(_4\)(\(v_4\)) followed by a slower collisional relaxation. The total quenching rate of Cl\(^*\) is reflected in the rise of the \(v_4\) fluorescence signal. The Cl\(^*\) total bimolecular quenching rate coefficients (± 2σ) obtained in this study at 298 ± 2 K are (1.9 ± 0.5) \(\times\) 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for quenching by CH\(_4\) and (1.4 ± 0.9) \(\times\) 10\(^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) for CD\(_4\). These rate coefficients for CH\(_4\) and CD\(_4\) are approximately 6% and 50%, respectively, of the hard sphere value. Intensity measurements interpreted within this kinetic scheme indicate that the E-V channel for \(v_4\) mode excitation accounts for ≈30% of the total quenching of Cl\(^*\) by each of CH\(_4\) and CD\(_4\). It is remarkable that the E-V branching ratios are the same in both systems even though the \(v_4 – Cl^*\) energy differences span a four-fold range from approximately \(\frac{1}{2}kT\) (CD\(_4\)) to 2kT (CH\(_4\)).