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AIMD Study of the Dynamics on S_1 and S_2 Excited States of Phosgene Derivatives (X_2CY; X=F, Cl; Y=O, S)

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The spectroscopic properties of phosgene derivatives ($X_2C=Y$, X=F, Cl; Y=O, S) are studied by using the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) method. Not only their ground (S_0) but also excited electronic states including lowest triplet state (T_1) and the lowest two excited singlet states (S_1 and S_2) are studied. The potential energy surface (PES) of possible dissociation channels of the states are also obtained by the EOM-CC method. Then the short time dynamics, up to several hundreds of femto-seconds, after the photo-absorption from the ground (S_0) state to each excited states (S_1 and S_2) are studied by applying an *ab initio* molecular dynamics (AIMD) method that combines the EOM-CC method for electronic structure and the semi-classical propagation method of frozen Gaussian wave-packets. The change of the autocorrelation function in time domain is obtained by computing the overlap between the initial wavepacket and the time-evolving wavepacket. The electronic absorption and fluorescence spectra of the excited states are simulated by the Fourier transformation of the autocorrelation function. The exceptional stability of the S_2 state of thiophosgene ($Cl_2C=S$), which is responsable to the anti-Kasha's fluorescence is reinvestigated by studying the dynamics on the S_2 state with the AIMD method. The dissociations and lifetime of the S_2 state of other phosgene derivatives as well as the possibility to observe the similar the anti-Kasha's fluorescence from other phosgene derivatives are also discussed.

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