

DIMINISHED CAGE EFFECT IN *p*-H₂: INFRARED SPECTRA OF CH₃S OBSERVED FROM PHOTOLYSIS OF CH₃SH, CH₃SCH₃, AND CH₃SSCH₃ ISOLATED IN *p*-H₂

YUAN-PERN LEE, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*; MOHAMMED BAHOU, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan*.

We report infrared absorption spectrum of the methylthio (or thiomethoxy) radical, CH₃S, isolated in solid *p*-H₂. CH₃S was produced by in situ UV photodissociation of three precursors: CH₃SH, CH₃SCH₃, and CH₃SSCH₃ isolated in solid *p*-H₂. New absorption features commonly observed with similar intensity ratios in experiments using these precursors are assigned as absorption of CH₃S. In addition to the previously assigned transitions of ν_3 (a₁) at 727.1 cm⁻¹, fundamental transitions ν_6 (a₁) at 771.1, ν_6 (e) at 1056.6, ν_5 (a₁) at 1400.0, and ν_4 (a₁) at 2898.0 cm⁻¹ were observed. The wavenumbers of these features agree satisfactorily with those predicted with a spin-vibronic Hamiltonian accounting for the anharmonic effects and the Jahn-Teller effects to the quartic term;^a the corresponding wavenumbers predicted from theory are ν_6 (a₁) at 793, ν_6 (e) at 1105, ν_5 (a₁) at 1436, and ν_4 (a₁) at 2938 cm⁻¹, with deviations of 1.4-4.6 % from experiments. Previous attempts of UV photolysis of CH₃SCH₃ and CH₃SSCH₃ isolated in an Ar matrix failed to produce CH₃S. These results serve as an excellent example that the diminished cage effect of solid *p*-H₂ makes production of free radicals via photolysis in situ feasible. If time permits, other examples will be discussed.

^aA. V. Marenich and J. E. Boggs, *J. Chem. Theory Comput.* **1**, 1162 (2005).