DIMINISHED CAGE EFFECT IN p-H_2: INFRARED SPECTRA OF CH_3S OBSERVED FROM PHOTOLYSIS OF CH_3SH, CH_3SCH_3, AND CH_3SSCH_3 ISOLATED IN p-H_2

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We report infrared absorption spectrum of the methylthio (or thiomethoxy) radical, CH_3S, isolated in solid p-H_2. CH_3S was produced by in situ UV photodissociation of three precursors: CH_3SH, CH_3SCH_3, and CH_3SSCH_3 isolated in solid p-H_2. New absorption features commonly observed with similar intensity ratios in experiments using these precursors are assigned as absorption of CH_3S. In addition to the previously assigned transitions of ν_3 (a_1) at 727.1 cm^{-1}, fundamental transitions ν_6 (a_1) at 771.1, ν_6 (e) at 1056.6, ν_5 (a_1) at 1400.0, and ν_4 (a_1) 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 (a_1) at 793, ν_6 (e) at 1105, ν_5 (a_1) at 1436, and ν_4 (a_1) at 2938 cm^{-1}, with deviations of 1.4-4.6 % from experiments. Previous attempts of UV photolysis of CH_3SCH_3 and CH_3SSCH_3 isolated in an Ar matrix failed to produce CH_3S. These results serve as an excellent example that the diminished cage effect of solid p-H_2 makes production of free radicals via photolysis in situ feasible. If time permits, other examples will be discussed.

[a] A. V. Marenich and J. E. Boggs, *J. Chem. Theory Comput.* **1**, 1162 (2005).