

パラ水素固体の中に単離したプロトン化 CO₂、OCS、CS₂ の 赤外吸収スペクトル

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Infrared spectra of protonated CO₂, OCS, and CS₂ in solid *para*-H₂
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ABSTRACT: In this work we produced protonated CO₂, OCS, and CS₂ in solid *para*-hydrogen (*p*-H₂) on electron bombardment during deposition of the sample mixtures at 3.2 K and measured infrared spectra. Spectral assignments were made based on expected chemistry and comparison of observed and predicted wavenumbers, infrared intensities, and isotopic ratios. Significant red shifts of OH stretching wavenumbers of HOCO⁺ and HOCS⁺ in solid *p*-H₂ from gaseous phase were observed while, in HSCO⁺ and HSCS⁺, HS stretching wavenumbers agreed well with those predicted theoretically for bare ions.

We have recently developed a new method to investigate the infrared (IR) spectra of protonated species by using electron bombardment during deposition of a *para*-hydrogen (*p*-H₂) matrix. [1] The bombardment of *p*-H₂ with electrons produces H₃⁺ and H via H₂ + e⁻ → H₂⁺ + 2e⁻ and H₂⁺ + H₂ → H₃⁺ + H reactions. Proton transfer from H₃⁺ to embedded molecules produces protonated species trapped in a *p*-H₂ matrix. This method has been applied to produce series of protonated polycyclic aromatic hydrocarbons as well as proton bound rare-gas dimers [RgHRg']⁺ (Rg, Rg' = Xe or Kr), among which asymmetric protonated rare-gas dimer XeHKr⁺ was characterized for the first time. [2, 3]

In this work, we applied this method to protonate small molecules CO₂, [4] OCS, [5] and CS₂, [6] whose existence in the interstellar media are known or predicted. In electron-bombarded CO₂/*p*-H₂ mixtures, after the matrix was maintained in darkness for prolonged period, intensities of absorption features of *t*-HOCO⁺ at 2403.5 (ν_1), 2369.9 (ν_2), 1018.1 (ν_4), and 606.5 (ν_6) cm⁻¹ decreased due to neutralization by electrons solvated in solid *p*-H₂. The assignments were made according to expected chemical behavior, observed isotopic shifts and comparisons with vibrational wavenumbers and relative intensities of previous reports and calculations with the B3PW91/aug-cc-pVQZ method. The ν_1 line of *t*-HOCO⁺ in solid *p*-H₂ (2403.5 cm⁻¹), similar to the line at 2673 cm⁻¹ of *t*-HOCO⁺ tagged with an Ar atom [7], is significantly red-shifted from that reported for gaseous *t*-HOCO⁺ (3375.37 cm⁻¹) [8] due to partial proton sharing between CO₂ and H₂ or Ar.

Similar red shift of OH stretching wavenumber was seen for HOCS⁺, [5, 9] but not for HS stretching wavenumber of HSCO⁺. Intuitively, the extent of proton sharing might be scaled by a difference of proton affinity between embedded molecule (i.e., CO₂, OCS, and CS₂) and H₂. However, proton affinity of OCS forming HOCS⁺ (610 kJ mol⁻¹) and HSCO⁺ (632 kJ mol⁻¹) is similar each other as compared to that of H₂ (422 kJ mol⁻¹), suggesting that the proton affinity is not the sole parameter that determines the red shift. The small or negligible shift in HSCO⁺ can be explained through an interaction energy -4.7 kJ mol⁻¹ between H₂ and HSCO⁺ much smaller than -17.3 kJ mol⁻¹ between H₂ and HOCS⁺.

Furthermore, we found that H atom in HOCS⁺ has more proton character and consequently neighboring H₂ molecules interact with the H atoms of HOCS⁺ more strongly than that of HSCO⁺ to induce a greater shift.

In the case of protonated CS₂, the wavenumber of the HS stretching mode of HSCS⁺ in solid *p*-H₂ (2477.2 cm⁻¹) is similar to the anharmonic wavenumber of HSCS⁺ (2424 cm⁻¹) predicted with the B3LYP/aug-cc-pVTZ method, indicating that the sharing of a proton between HSCS⁺ and neighboring H₂ molecules is insignificant, similarly to HSCO⁺. Actually, the calculated interaction energy between H₂ and HSCS⁺ was quite small -0.4 kJ mol⁻¹, consistent with the observation.

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