diation. The ultraviolet (280 to 290 $m\mu$) and visible bands grow parallelly, suggesting that the two bands arise from the same species. The color is stable for at least 3 to 5 hours at $-80°C$. Though fading is apparent at higher temperatures, color is still detectable after 45 minutes at $-20°C$. In experiments with the water clathrate of (CCl_4, H_2S) color develops with the sample held between $-10°$ and $-2°C$ during irradiation. Color stability here is the order of 1 or 2 minutes.

These observations can be interpreted in terms of reactive species located in cavities of the water clathrate. In the CH_3SH clathrate CH_3S is assumed to be stabilized. This is produced by the following reactions (6):
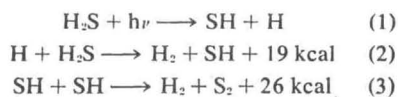
$$CH_3SH + h\nu \longrightarrow CH_3S + H$$
$$H + CH_3SH \longrightarrow CH_3S + H_2$$
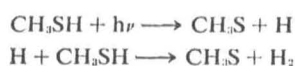
Similarly, C_2H_5S resides in the cavities of its parent clathrate. Evidence in support of these assignments comes from the work of Rosengren, who shows that photolysis of mercaptans in hydrocarbon glasses at $77°K$ produces absorptions with λ_{max} at 400 $m\mu$ which are assigned to RS radicals (7). My experiments in polar glass with CH_3SH provide independent confirmation of Rosengren's results.

The observed temperature stability of the absorption bands reinforces the hypothesis that the radicals occupy clathrate cavities. Though diminished in intensity, the 310- and 370-$m\mu$ bands survive annealing at $-20°C$ for 40 minutes.

It is not likely that CH_3S and C_2H_5S will disproportionate in their cavities. The absorptions assigned here to these radicals are unlike those reported for products of thiyl radical disproportionation (8).

In the H_2S clathrates the stabilized species is assumed to be S_2. This is produced by the following reactions (9):

$$H_2S + h\nu \longrightarrow SH + H \quad (1)$$
$$H + H_2S \longrightarrow H_2 + SH + 19 \text{ kcal} \quad (2)$$
$$SH + SH \longrightarrow H_2 + S_2 + 26 \text{ kcal} \quad (3)$$

The radius of escape from the cavities varies from 1.0 to 1.5 Å, depending on cavity size (10). SH is too large (radius = 1.7 Å) to diffuse interstitially. After dissociation, however, the products possess sufficient kinetic energy to distort the hydrogen bonded lattice, permitting SH to pass from the parent cage into a neighboring one and to react according to reaction 3 (11). Evidence in support of S_2, one of the

known products of photolyzed H_2S, as the absorbing species in Fig. 1 is drawn from (i) the maximum in the ultraviolet absorption of Fig. 1 at 280 to 290 $m\mu$ which falls near the position of the strongest absorption bands of the ν',o progression of S_2 (12) and (ii) the absorption band with $\lambda_{max} = 507$ $m\mu$ reported in low temperature deposits of S_2 (13). This band falls reasonably close to the 520 and 560 $m\mu$ bands of the water clathrates of H_2S. Higher polymers of sulfur (for example, S_6 and S_x) can probably be ruled out of consideration because their absorption characteristics (14) do not fully satisfy both i and ii.

The stability of color at relatively high temperatures also supports the view that the active species is stabilized in the cavities.

The spectral differences between the single and double water clathrates of H_2S may originate in structural differences between the hydrate types. Single hydrates all form in a cubic lattice of 12 Å unit cell edge with two sizes of cavity: 5.2 Å and 5.9 Å free diameters. The double hydrates form also in a cubic symmetry, of unit cell edge 17.3 Å, again with two sizes of cavity: 4.8 Å and 6.9 Å (15). Thus S_2 resides in a cavity of different size according to the structure of the water clathrate from which it was formed. Consequently the S_2 energy levels experience a matrix shift relative to the gas phase spectrum, the magnitude of shift depending on cavity size. Concentrations of stabilized species cannot be given at the present time (16).

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