

Phase Transitions in the Hydroquinone Hydrogen Sulfide Clathrate Compound*

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Abstract. Heat capacities of $[C_6H_4(OH)_2]_3 \cdot (H_2S)_x$ were measured between 1 and 15 K. Heat capacity peaks were found at (7.56 ± 0.09) K, (7.61 ± 0.05) K, and (7.65 ± 0.07) K for the compounds with $x = 0.92, 0.95,$ and 0.96 . A weak anomaly was observed around 6.75 K for the compound with $x = 0.85$. The temperatures of these anomalies are unusually low among the phase transitions of molecular crystals. The decrease of the transition temperature from that of crystalline H_2S ($= 103.52$ K) is a clear indication of the effect of enclathration on the molecular interaction. A comparison of the rotational heat capacity of the trapped hydrogen sulfide molecules with that of crystalline hydrogen sulfide shows that the trapped hydrogen sulfide molecules have a large rotational freedom at low temperatures (~ 13 K). This agrees with the results from far infrared spectroscopic data. The dielectric constant of the clathrate compound obeyed the Curie–Weiss law above 30 K and no significant dielectric loss was found over the whole temperature range. These results showed that the trapped hydrogen sulfide molecules execute free rotation or are orientationally disordered above ~ 20 K.

Key words: clathrate, hydroquinone hydrogen sulfide clathrate compound, phase transition, molecular rotation, heat capacity, dielectric constant.

1. Introduction

Clathrate systems offer interesting possibilities for studying the dynamics of molecular movements and intermolecular interactions in a well characterized condition. The guest molecules are in a surrounding which is often the same for all the guest molecules. The fact that each molecule occupies a cavity allows it to be isolated from its neighbors. The dynamical aspects of the molecular freedom in clathrates have been investigated by several authors by heat capacity measurements [1–5]. In 1956, van der Waals assumed, in his statistical theory of the inclusion phenomenon, that the interactions among the trapped molecules were negligibly small [6]. This is an adequate assumption in most cases. However, Matsuo *et al.* found phase transitions in the hydrogen cyanide [7] and methanol [8] clathrate compounds, which experimentally showed that interactions exist between the guest molecules and that these interactions are strong enough to reveal themselves in the bulk properties of the substance.

From these previous studies we can form a coherent picture of the dynamical state of a guest molecule in the cavity. It has three translational degrees of freedom, each of which can be described as a rattling motion. Angular degrees of freedom exist for polyatomic guests. In most cases, the angular motion is described as hindered rotation in the cavity. The mutual orientation of neighboring guests is important when they are strongly polar and the temperature sufficiently low, and gives rise to phase transitions. The present investigation aims at an

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extension of the above research to smaller guest molecules with their small moments of inertia and deals with the hydroquinone clathrate of hydrogen sulfide, $3Q \cdot (H_2S)_x$, where Q represents hydroquinone, $C_6H_4(OH)_2$.

2. Experimental

The hydroquinone hydrogen sulfide clathrate compounds were prepared as described in the literature [9].

The occupancy of the cavities was determined by elemental analysis of sulfur as follows. About 4 mg of the sample was burnt in O_2 . The sulfuric acid thus formed was titrated with barium perchlorate solution using carboxy arsenazo as the indicator. The occupancy determined in this way was reproducible to $\pm 3\%$.

The heat capacity measurements were carried out between 1 and 15 K on four specimens whose cavity occupancies were 0.85, 0.92, 0.95, and 0.96. The uncertainties of these cavity occupancies were ± 0.03 . A nonadiabatic low temperature calorimeter using liquid 3He as the coolant [10] was employed for this temperature region. For $3Q \cdot (H_2S)_{0.95}$, the heat capacity was measured between 13 and 300 K. An adiabatic low temperature calorimeter with a built-in cryorefrigerator was used to cover this temperature region. Details of this apparatus have already been described [11].

The dielectric constants were measured at 1 kHz on two specimens whose cavity occupancies were 0.95 ± 0.03 (polycrystalline) and 1.00 ± 0.03 (single crystal). The measurements were carried out between 4.2 and 300 K.

3. Results and Discussion

Figure 1 shows the heat capacities of the $3Q \cdot (H_2S)_{0.95}$ sample per three moles of hydroquinone in the entire temperature range. The heat capacity peak occurred at (7.61 ± 0.05) K and the heat capacities above this temperature had the usual sigmoidal temperature dependence, except at 273 K where a peak due to the melting of the ice occluded in the crystal occurred (not shown in the figure). A small correction for the heat capacity of the ice was applied to the experimental values. The heat capacities of the four specimens between 1 and 15 K are shown graphically in Figure 2. The deviations from the smooth lines drawn through the experimental points are about 3% at 15 K. The heat capacity peaks occurred at (7.56 ± 0.09) , (7.61 ± 0.05) , and (7.65 ± 0.07) K for the samples with $x = 0.92, 0.95,$ and 0.96 , respectively. A weak anomaly was found around 6.75 K for the sample with $x = 0.85$.

It is assumed that the heat capacity of the clathrate consists additively of the contributions from the host lattice and the guest molecules [12]. In the clathrate cavity, the guest molecule executes a rattling motion and this motion is appropriately described by the Pöschl-Teller potential [13]. The two parameters involved in this potential function were derived from spectroscopic data. For the hydrogen sulfide clathrate, Barthel *et al.* [14] have observed two bands at 57 and 74 cm^{-1} at 18 K in the far infrared spectrum and Anthonson [15] has observed one band at 45 cm^{-1} at 93 K in the Raman spectrum. They assigned these bands to the rattling motion of the trapped hydrogen sulfide molecules. In order to calculate the heat capacity due to the rattling motion, the partition function was taken to be the product of three partition functions each in one dimension. The rotational heat capacity of the trapped hydrogen sulfide molecules was obtained by subtracting the contributions due to the host lattice and the rattling motion of the guest molecules from the experimental values. The calculated values are shown in Figure 3. These are compared with the heat capacity of

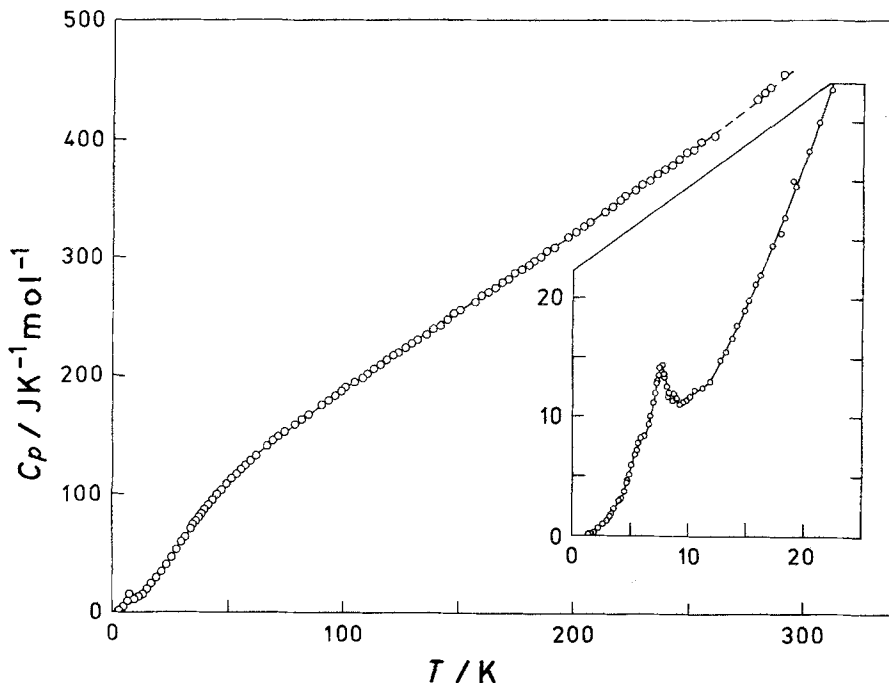


Fig. 1. Heat capacity of $[C_6H_4(OH)_2]_3 \cdot (H_2S)_{0.95}$.

crystalline hydrogen sulfide [16]. The large heat capacity of the enclathrated hydrogen sulfide shows that the density of states available to the molecules increases on enclathration. In the far infrared spectrum a strong absorption around 22 cm^{-1} (at 10 K) was assigned to the rotational transition in the cavity [17, 18]. The heat capacity data are consistent with the existence of the low lying energy levels, even though the level scheme may be more complicated than that for free rotation because of the anisotropic crystal field, rotation-translation interaction and inter-guest effects.

It is of interest to compare the heat capacity anomaly with those of the similar clathrate compounds containing hydrogen cyanide and methanol. Equating the nearest neighbor dipole-dipole interaction energy with the transition temperature, we obtain the following expression;

$$kT_c = \frac{2\mu^2}{4\pi\epsilon'_\infty\epsilon_0 r^3}, \quad (1)$$

where k is the Boltzmann constant, T_c the phase transition temperature, μ the dipole moment of the guest molecule, ϵ'_∞ the high frequency dielectric constant of the clathrate compound, and r the distance between the nearest guest molecules along the c -axis. ϵ'_∞ was taken to be 3.2, the dielectric constant of the hydroquinone acetylene clathrate compound [19]. A comparison of the calculated and observed T_c values are given in Table I. The nearest-neighbor distance in the hydrogen cyanide compound was taken to be equal to that in the hydrogen sulfide compound. The transition temperatures are reproduced reasonably well by the dipole-dipole interactions for the hydrogen cyanide and methanol compounds. However, the same calculation predicts the transition temperature to be 4.8 times as large as the temperature of

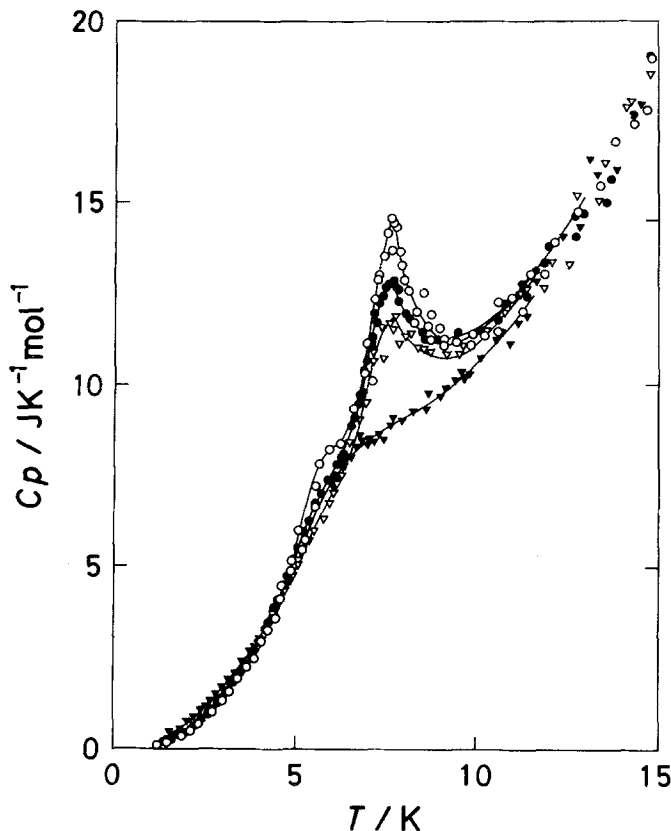


Fig. 2. Heat capacities of $[\text{C}_6\text{H}_4(\text{OH})_2]_3 \cdot (\text{H}_2\text{S})_x$. — \blacktriangledown —; $x = 0.85$. — ∇ —; $x = 0.92$. — \circ —; $x = 0.95$. — \bullet —; $x = 0.96$.

the heat capacity anomaly in the hydrogen sulfide compound. This probably reflects the small crystal field strength in the hydrogen sulfide clathrate compounds. In the first two compounds, the guest molecules will be preferentially oriented in stable orientations relative to the crystal axis because of their elongated molecular shapes [22]. The maximum dipole energy embodied in Equation (1) is suitable in these cases. In the hydrogen sulfide system, the barrier to the rotation in the cavity is low. The dipole-dipole interaction has to be averaged over the angular coordinate. This will lead to a lower transition temperature. However, the magnitude of this effect has not been calculated quantitatively.

Figure 4 shows the real part of the dielectric constants ϵ'_r as a function of the temperature for the two samples with $x = 0.95$ (polycrystalline) and 1.00 (single crystal). The ϵ'_r values of these samples increased with decreasing temperature from room temperature to about 10 K and decreased at the lower temperatures. The dielectric data are consistent with the heat capacity data in regard to the absence of the phase transitions between about 10 K and room temperature. The quantity $\epsilon'_r/(\epsilon'_r - \epsilon'_\infty)(2\epsilon'_r + \epsilon'_\infty)$ is also shown in Figure 4 [23]. The linearity of this quantity against temperature shows that the trapped hydrogen sulfide molecules execute free rotation or are orientationally disordered. The barrier to rotation or reorientation of the molecule, if any, is very low, for the dielectric loss was insignificant in the whole temperature range, 4.2 to 300 K.

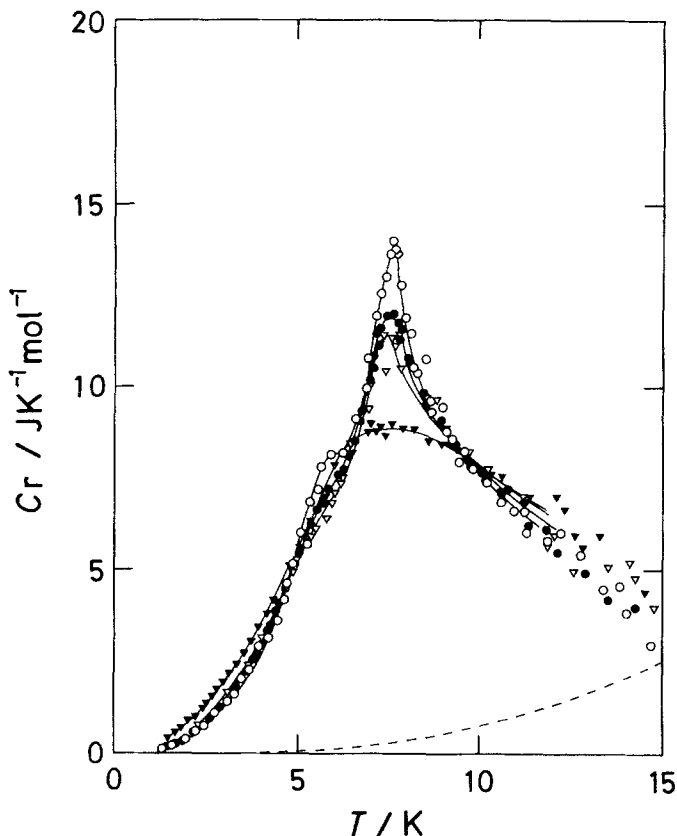


Fig. 3. Rotational heat capacities of one mole of hydrogen sulfide trapped in the clathrate compounds $[C_6H_4(OH)_2]_3 \cdot (H_2S)_x$. \blacktriangledown —; $x = 0.85$. ∇ —; $x = 0.92$. \circ —; $x = 0.95$. \bullet —; $x = 0.96$. ----; the heat capacity of crystalline H_2S [16].

Table I. Comparison of the observed and calculated peak temperatures

Guest	$\mu(3.3356 \times 10^{-30} \text{ Cm})$	$r(\text{nm})^a$	$T_c(\text{obs})$ K	$T_c(\text{calc})$ K ^c	$\frac{T_c(\text{calc})}{T_c(\text{obs})}$
HCN[7]	2.95[19]	0.552 ^b	178[7]	234.2	1.32
CH ₃ OH[8]	1.66[19]	0.556[21]	67[8]	73.0	1.09
H ₂ S	1.17[20]	0.552[9]	7.6	36.8	4.84

^a The distance between guest molecules along the c -axis.

^b The value of r of the HCN system was assumed to be equal to that of the H_2S system.

^c $T_c(\text{calc}) = 2\mu^2/4k\pi\epsilon'_\infty\epsilon_0 r^3$.

Below 30 K the dielectric constant deviates from the classical Curie-law behavior. Two factors may be responsible for this behavior. One is the quantum effect. Since the low lying energy levels of a freely rotating hydrogen sulfide molecule are $10\text{--}20 \text{ cm}^{-1}$ apart, the quantum effects will have to be taken into account to describe its response to the electric field. Such a calculation [24] showed that the dielectric constant flattens off at the lowest temperature in contrast to the classical behavior which diverges as $1/T$. The other is the interaction

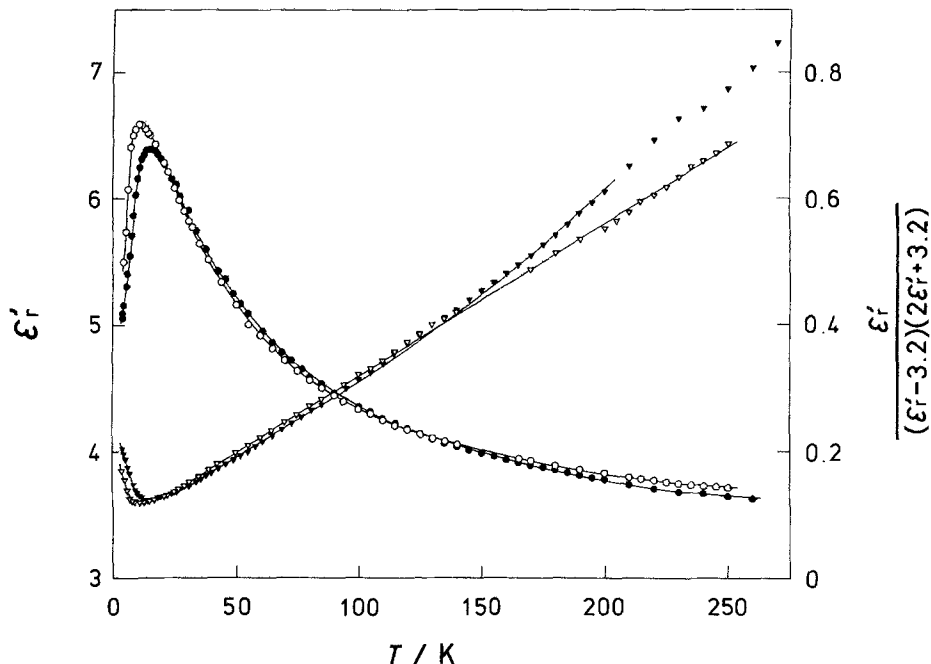


Fig. 4. Real part of the dielectric constant of $[\text{C}_6\text{H}_4(\text{OH})_2]_3 \cdot (\text{H}_2\text{S})_x$. —●—; $x = 0.95$ (polycrystalline), —○—; $x = 1.00$ (single crystal); ϵ'_r plotted against temperature: —▼—; $x = 0.95$ (polycrystalline), —▽—; $x = 1.00$ (single crystal); $\epsilon'_r / (\epsilon'_r - 3.2)(2\epsilon'_r + 3.2)$ plotted against temperature.

between the guest molecules. Even though the temperatures of the maximum dielectric constant and the heat capacity peak do not coincide exactly, they are close enough for us to suspect that they have a common origin: orientational ordering of the hydrogen sulfide molecules. It will be of interest to extend the crystal structure study to very low temperatures.

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References

1. N. G. Parsonage and L. A. K. Staveley: *Mol. Phys.* **2**, 212 (1959).
2. N. G. Parsonage and L. A. K. Staveley: *Mol. Phys.* **3**, 59 (1960).
3. N. R. Gray, N. G. Parsonage, and L. A. K. Staveley: *Mol. Phys.* **4**, 153 (1961).
4. N. R. Gray and L. A. K. Staveley: *Mol. Phys.* **7**, 83 (1963).
5. G. L. Stepakoff and L. V. Coulter: *J. Phys. Chem. Solids* **24**, 1435 (1963).
6. J. H. van der Waals and J. C. Platteuw: *Adv. Chem. Phys.* **2**, 1 (1959).
7. T. Matsuo, H. Suga, and S. Seki: *J. Phys. Soc. Jpn.* **30**, 785 (1971).
8. T. Matsuo: *J. Phys. Soc. Jpn.* **30**, 794 (1970).
9. T. C. W. Mak, J. S. Tse, Chi-sang Tse, Ka-sing Lee, and Yuet-han Chong: *J. Chem. Soc. Perkin Trans. 2*, 1169 (1976).
10. N. Arai, M. Sorai, H. Suga, and S. Seki: *Bull. Chem. Soc. Jpn.* **50**, 1702 (1977).

11. K. Moriya, T. Matsuo, and H. Suga: *J. Chem. Thermodyn.* **14**, 1143 (1982).
12. H. Ukegawa, T. Matsuo, and H. Suga: *Solid State Commun.* **52**, 203 (1984).
13. E. Bartholomè and A. Eucken: *Trans. Faraday Soc.* **33**, 45 (1937).
14. C. Barthel, X. Gerbaux, and A. Hadni: *Spectrochim. Acta* **A26**, 1183 (1970).
15. J. W. Anthonsen: *Acta Chem. Scand.* **A29**, 179 (1975).
16. W. F. Giauque and R. W. Blue: *J. Am. Chem. Soc.* **58**, 831 (1936).
17. X. Gerbaux, C. Barthel, A. Hadni, and M. Mohan: *Spectrochim. Acta* **A29**, 1965 (1973).
18. X. Gerbaux, C. Barthel, and A. Hadni: 'Molecular Spectroscopy of Dense Phases', in *Proc. 12th Eur. Congr. Mol. Spectrosc. 1975*, (Ed. M. Grosmann), p. 417.
19. J. S. Dryden: *Trans. Faraday Soc.* **49**, 1333 (1952).
20. M. Davies and K. Williams: *Trans. Faraday Soc.* **64**, 529 (1968).
21. T. C. W. Mak: *J. Chem. Soc., Perkin Trans. 2*, 1435 (1982).
22. J. A. Ripmeester, R. E. Hawkins, and D. W. Davidson: *J. Chem. Phys.* **71**, 1889 (1979).
23. C. J. F. Böttcher: *Theory of Electric Polarization*, p. 253. Elsevier, Amsterdam (1973).
24. J. H. van Vleck: *The Theory of Electric and Magnetic Susceptibilities*, p. 185. Oxford Univ. Press, London and New York (1932).