Clathrate Formation and Phase Transitions in β-Hydroquinone⋆

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Abstract. Clathrate thermodynamic stability conditions and the phase transitions associated with either the orientational ordering of the guest molecules or with the condensation of the guest molecules in the host lattice are investigated by means of the common microscopic model. The theory proposed describes the thermodynamic properties of β-hydroquinone (Q_β) clathrates. The dielectric constant $\varepsilon(T)$ was measured experimentally in $Q_\beta \cdot CH_3OH$ and $Q_\beta \cdot SO_2$ in the temperature range from 4.2 to 300 K and the phase transitions were found. It is shown that the theory qualitatively explains the experimental data obtained.

1. Introduction

A large number of clathrates formed by various hosts and guests are known today [1–3]. Among them, there is a large class of compounds with metastable empty host lattices [3]. The basis for their investigation was laid by H. M. Powell in his pioneering work which is reviewed in [1]. H. M. Powell not only managed to determine the structure of the typical representatives of this clathrate class − β-hydroquinone (Q_β) with guests $G = SO_2$ and CH_3CN − but also to point out the theoretical problems that were to be solved in order to understand properly the physico-chemical properties of clathrates. One of the problems dealt with the investigation of the microscopic mechanisms that are responsible for the formation of thermodynamically stable compounds. Particular attention has been paid to the solution of this complicated problem (mainly for $Q_\beta \cdot G$ clathrates) [4–9].

The first statistical theory that estimated concentration $c(P, T)$ (here, T is the temperature, P the pressure) of the gas in $Q_\beta \cdot G$ was proposed by van der Waals and Platteeuw [4]. Considering the clathrate as a gas solution in the crystal, existing in thermodynamic equilibrium with the solid and gaseous phases, they determined the conditions for stable clathrate formation. They pointed out that, in $Q_\beta \cdot G$, at normal pressure and temperature $T \approx 300$ K, the limiting concentration c is equal to 0.34. This result is in agreement with the experimental data when the guests are rare gases. But, in order to explain the existence of clathrates with $c > 0.34$, it is necessary to modify the theory [4], especially when the guests (e.g. $G = CH_3OH$, HCl, SO_2, etc.) slightly modify the form of the Q_β cavity [1].

In this connection, some authors [5–10] have assumed that the interactions among the guests influence the clathrate formation process. The most complete theoretical calculation of the concentration characteristics in $Q_\beta \cdot G$ was carried out in [7]. In this paper, the geometric location of the cavities was taken into account. It was shown that the inclusion of the interactions among the guests is a necessary, but also insufficient, criterion to explain the thermodynamic stability of $Q_\beta \cdot G$ with $c > 0.34$. Besides these interactions, one has to take

⋆ Dedicated to Professor H. M. Powell.

into consideration the guest-host and host-host interactions as well as a finite number of the guest molecule orientations in the cavity. The authors of [7, 8] showed that, in accordance with these conditions and at $T \approx 300$ K, the concentration values can vary from 0.34 to 1.

The important results obtained in a series of experimental studies [11–15] (see also [9]) helped to explain some physical properties of clathrates. In these studies, phase transitions (PT) have been found in $Q_\beta \cdot G$ and hydrates. PT's were caused by ordering of the guest molecules in the cavities. Thus, the assumption that the interactions among the guests must be taken into account was proved and the PT theory became a necessity for clathrates. In order to solve this problem, the problem of the thermodynamic stability characterizing the specific features of clathrates should also be taken into account. But there has been no theory proposed that would explain, from the common point of view, the clathrate formation process and the PT in these compounds.

In this paper, by means of microscopic models [7, 8], a theory is proposed which allows us to investigate, simultaneously, the stability and PT of clathrates. Using experimental methods we have also obtained the temperature dependence of the dielectric constant $\varepsilon(T)$ in the clathrates $Q_\beta \cdot SO_2$ and $Q_\beta \cdot CH_3OH$.

2. Theory

We examined the host lattice with N_k various closed cavities of the $k = 1, 2, \ldots$ type. The cavities can vary according to their shape, dimensions, measurements, stoichiometric coefficient, etc. $\Sigma_k N_k = N$ is the common number of cavities in the host lattice. We have assumed that a guest molecule can be orientated among the $q \geqslant 2$ equilibrium states in the cavity and that any cavity can never hold more than one guest molecule. We have introduced pair interaction potentials between the guests (cavities) of the i and k-types. These potentials consist of two parts – the multipole (dipole, quadrupole, octopole, etc...) interactions $I_{ik}^{\xi\zeta}(\mathbf{r} - \mathbf{r}')$ and dispersion interactions $v_{ik}(\mathbf{r} - \mathbf{r}')$; here $\mathbf{r}, \mathbf{r}'$ are the cavity centre coordinates and indices $\xi, \zeta = 1, 2, \ldots, q$ show the number of possible orientations of the guest molecule in the cavity. The Hamiltonian of the system consisting of the gas molecule solution in the crystal can be written

$$\mathscr{H} = -\frac{1}{2} \sum_{\mathbf{r}\mathbf{r}'ik} \eta_\mathbf{r}^i \eta_{\mathbf{r}'}^k \left[I_{ik}^{\xi\zeta}(\mathbf{r} - \mathbf{r}') e_\mathbf{r}^\xi e_{\mathbf{r}'}^\zeta + v_{ik}(\mathbf{r} - \mathbf{r}') \right] -$$
$$- \sum_{\mathbf{r}i} B_i \eta_\mathbf{r}^i - \sum_{i\xi\mathbf{r}} \Delta_\xi \eta_\mathbf{r}^i - \sum_{i\mathbf{r}} \mu_i \eta_\mathbf{r}^i. \tag{1}$$

Here, $e_\mathbf{r}^\xi$ is the operator [17] that is equal to 1 if the guest molecule of the i-type is orientated towards position ξ in the cavity with coordinate $\mathbf{r}$ and is equal to zero in all the remaining cases, e.g., if $q = 2$, then $e_\mathbf{r}^\xi \equiv \frac{1}{2}(1 + \sigma_\mathbf{r}^z)$ where $\sigma_\mathbf{r}^z = \pm 1$ is the Pauli operator. B_i is the energy difference between the full and empty i-type cavities. The values of $\eta_\mathbf{r}^i$ describe the distribution of the guest molecules over the cavities. Asymmetry parameter Δ_ξ shows that all the orientations of the guest molecule can be inequivalent (when $\Delta_\xi = 0$, we have q equivalent orientations) and μ_i is the chemical potential of the ith component in the solution.

The Hamiltonian (1) can be used to describe any crystalline clathrate system with a finite number of guest molecule orientations in the cavities, e.g., if we have two types of cavities in the lattice (as in gas hydrates [1, 3]), but one type of the guest molecules, then $i, k = 1, 2, 3$ and indices $i, k = 1, 2$ belong to the empty cavities while $i, k = 3$ belong to the occupied ones. When we have two types of guests, $i, k = 3, 4$ and so on.

In order to find the clathrate thermodynamic stability conditions, one must know the chemical potential μ_{Q_k} of the k-type host molecules and the chemical potential $\mu_{G_i}^\beta$ of the i-type

guest molecules in a clathrate. Taking into account the application of the latter theory to the clathrates $Q_\beta \cdot G$, we calculated μ_{Q_k} and $\mu_{G_i}^\beta$ for β-hydroquinone.

There is only one cavity type in $Q_\beta \cdot G$. Thus, we take $i, k = 1$ if the cavity is filled with guest G and $i, k = 2$ if it is empty. Then the guest concentration in a clathrate is $c_1 = \langle \eta_r^1 \rangle$ and, correspondingly, the concentration of the empty cavities $c_2 = 1 - c_1 = \langle \eta_r^2 \rangle$ where the brackets $\langle \ldots \rangle$ mean the statistical average with the Hamiltonian (1). In order to carry out the concrete calculations one must know the elements of the $q \times q$ matrix $I^{\xi\zeta}$, which depends on the symmetry of the lattice, the geometric form of the guest, and on other factors. To simplify the problem, we have chosen $I^{\xi\zeta}$ to be of the Potts type [17]: $I^{\xi\zeta} = I^{(1)}$ if it describes the interactions between the parallel-oriented guests; $I^{\xi\zeta} = I^{(2)}$ in all the remaining cases. Then, the product $e^\xi e^\zeta$ can be written as follows

$$e^\xi e^\zeta = \frac{1}{q} \sum_{l=1}^{q-1} \xi^l \zeta^{q-l} \tag{2}$$

where ξ and ζ attain the values $1, \omega, \omega^2, \ldots, \omega^{q-1}$, with $\omega = \exp(2\pi i/q)$ [17]. The free energy of a cavity of the guest-host system is equal to

$$F = \Omega + \sum_i \mu_i c_i \tag{3a}$$

$$\Omega = -\frac{T}{N} \ln Sp \exp(-\beta \mathcal{H}) \tag{3b}$$

where $\beta = 1/T$. The expression of the dependence of μ_i on c_i can be found using the equality

$$c_i = -\frac{\partial \Omega}{\partial \mu_i}. \tag{4}$$

In order to understand the qualitative behaviour of clathrates during the PT, we used the molecular field approximation [8, 16]. For the sake of simplicity, we assumed also that $\Delta_\xi = 0$. Then the expression for the free energy becomes

$$F = F_\beta + \left(\frac{q-1}{q}\right) Ic^2 s^2 - \frac{c^2 v}{2} -$$
$$- T[c \ln(Z/q) + c \ln c + (1-c) \ln(1-c)] + cB. \tag{5}$$

Here, F_β is the free energy of empty host lattice Q_β,

$$I = I_{11}^{(2)} - I_{11}^{(1)}, \qquad v = v_{11} + v_{22} - 2v_{12},$$

$$Z = e^{\beta\alpha_1} + (q-1) e^{-\beta\alpha_2}, \qquad \alpha_1 = \frac{q-1}{q} Isc, \quad \alpha_2 = \frac{Isc}{q},$$

$$c = c_1, \qquad B = v_{22} - v_{11} - B_1,$$

$$I_{11}^{(v)} = \sum_{\mathbf{r}} I_{11}^{(v)}(\mathbf{r}), \qquad v_{ik} = \sum_{\mathbf{r}} v_{ik}(\mathbf{r}). \tag{6}$$

In (5) and (6), $s = \langle e_r^\xi \rangle$ is the average value of a 'spin' characterizing the order of the guest molecules in the cavities and can be obtained from the equation

$$s = \frac{1 - \exp(-\beta Isc)}{1 + (q-1)\exp(-\beta Isc)}. \tag{7}$$

Using (4) and (5) we can obtain the expressions for the chemical potentials of host molecules μ_Q and guest molecules μ_G^β in the clathrate

$$\mu_Q = \frac{\partial F_\beta}{\partial N} + m(F - 2\mu c)$$

$$= \mu_Q^\beta + m\left[T\ln(1 - c) + \tfrac{1}{2}vc^2 + \tfrac{1}{2}\frac{(q - 1)}{q}Ic^2s^2\right],\tag{8a}$$

$$\mu_G^\beta = 2\mu = T\ln\left(\frac{c}{1 - c}\right) - T\ln(Z/q) - cv + B,\tag{8b}$$

where $\mu_1 = -\mu_2 = \mu$ and $m = \tfrac{1}{3}$ in Q_β.

If the clathrate is to occur in thermodynamic equilibrium, then [4]

$$\mu_Q = \mu_Q^\alpha.\tag{9}$$

Inserting (8a) into (9) we have

$$D = f\tag{10}$$

$$D = (\mu_Q^\alpha - \mu_Q)/m; \qquad f = T\ln(1 - c) + \frac{vc^2}{2} + \tfrac{1}{2}\frac{(q - 1)}{q}Ic^2s^2.$$

Equation (10) is the main equation determining the guest concentration in the clathrate. When $v = 0$, (10) gives the form of the corresponding equation in [4]. When $v/T \ll 1$, the following equation can be obtained from (10)

$$c = c_0(T) + c_1(T), \quad c_0(T) = 1 - \exp(D(T)/T)$$

$$c_1(T) \approx \frac{v}{2T}[1 - c_0(T)]^3.\tag{11}$$

It is noteworthy that v is the sum of the dispersion interactions of the guest-guest (v_{11}), guest-host (v_{12}), and host-host (v_{22}) types (see Equation (6)). For $Q_\beta \cdot G$, when $T = 298$ K, $D \approx -41$ K, and $v > 0$, it follows from (11) that $c > 0.34$. Thus, the inclusion of v allows us to understand the concentration values $c > 0.34$ in $Q_\beta \cdot G$.

2.1. CONCENTRATIONAL PHASE TRANSITIONS

In the beginning, the case when the guest molecules are disordered in the cavities ($s = 0$) was investigated. It follows from (10) that the function $f(c, T)$ can take different forms, depending on the relation between v and T.

Region I.

When $4T > v$ and c decreases from 1 to 0, $f(c)$ changes from $f(0) = 0$ to $f(1) = -\infty$.

Region II.

When $4T < v$, $f(c)$ has minimum and maximum at points $c_{1,2} = \tfrac{1}{2} \mp (\tfrac{1}{4} - T/v)^{1/2}$. If $f(c_1) < D < f(c_2)$, the PT can occur in the system. We supposed that, at $\tau = (v - 4T)/v > 0$

and $\tau \ll 1$, $D(T)$ crosses the curve $f(c, T)$ at points

$$c_{q1} = c_1 - x_1, \quad c_{q2} = c_1 + x_2, \quad c_{q3} = c_1 + x_3, \tag{12}$$

where $x_i \ll 1$. Then the equilibrium state of the clathrate occurs at such c_{qi} for which $\mu_G^{\beta}(c_{qi})$ from (8b) would be minimum. We determined $D(T) = \frac{1}{2}[f(c_1) + f(c_2)]$ and assumed that $B \approx B_0 - B'c(B'/B_0 \ll 1)$. Then it follows from the solution of Equation (10) (using also (8b) at $\tau \ll 1$) that when τ (or T) decreases, at the point

$$\tau_c \sim \left(\frac{B'}{v}\right)^{4/3} \ll 1 \tag{13}$$

the first-order PT from the value c_{q3} to the value c_{q1} occurs and $\Delta c_q(\tau_c) \sim (B'/v)^{1/3}$. The specific heat $C_P = -T(\partial^2 F/\partial T^2)_P$ in τ_c also shows a jump-like behaviour. This PT can be interpreted as a sudden 'exit' of a certain proportion of the guest molecules $\Delta c_q = c_{q3} - c_{q1}$ from the closed cavities. It is important that, both at c_{q3} and at c_{q1}, the clathrate becomes a thermodynamically-stable compound. Therefore, solid clathrate solutions $Q_\beta \cdot G$ can exist between c_{q1} and c_{q3}. The actual values of c_q strongly depend, most likely, on the sample preparation conditions because the parameter $B(c)$, in general, can be suddenly changed with changing of the crystallization conditions. In the same way, it can be shown that the first-order PT can occur at $s \neq 0$ between the states $c \lesssim 1$ ($s \neq 0$) and $c \lesssim 0.5$ ($s = 0$.)

2.2. ORIENTATIONAL PHASE TRANSITIONS

Firstly, let us analyse such T values when the guests in the cavities are orientationally disordered and $s = 0$. For the sake of simplicity, we investigated the case when Equation (10) has only one solution c_q. Then, when T decreases, the PT from state $s = 0$ to state $s \neq 0$ can occur and the guest molecules in the cavities become ordered. The expression for the PT temperature can be obtained from the equalisation of the free energies of both phases $F(T_c, c_q, s_c) = F(T_c, c_q, 0)$

$$T_c = \frac{c_q I(q - 2)}{2(q - 1)\ln(q - 1)}, \quad q > 2 \tag{14}$$

where the order parameter jump is given by

$$s_c = (q - 2)/(q - 1). \tag{15}$$

In comparison with other inclusion systems, clathrates have an interesting peculiarity: the value c_q in (14) may not be freely chosen but must be determined from the solution of Equation (10), i.e., $c_q = c_q(T, D)$.

The expressions for the main thermodynamic functions – specific heat C_P, transition entropy $S_C = -(\partial F/\partial T)_{T = T_c + 0}$ etc. – can be easily obtained from (5)–(10), e.g., we can obtain the dielectric constant

$$\varepsilon = \varepsilon_0 + \frac{4\pi p}{V_c} c \left(\frac{\mathrm{d}P_s}{\mathrm{d}E}\right)_{E \to 0} \tag{16}$$

Here $V_c = V/n$, V is the volume of the unit cell, n is the number of the cavities in the unit cell, p is the dipole moment of the guest molecule, ε_0 is the value of the dielectric constant at superhigh frequencies (usually, $\varepsilon_0 \gtrsim 1$). The polarization P_s is related to s by the following

equation

$$P_s = ps \frac{q - 1}{q}. \tag{17}$$

When we add the term $-pE \sum_{\mathbf{r}i} \eta_{\mathbf{r}}^i e_{\mathbf{r}}^\xi$ to the Hamiltonian (1), we obtain from (7), (16), and (17) at $E \to 0$

$$\varepsilon = \varepsilon_0 + ec(q - 1) \{T[(q - 1) \exp(-\beta Isc/2) +$$
$$+ \exp(\beta Isc/2)]^2 - qIc\}^{-1} \tag{18}$$

where $e = 4\pi p^2/V_c$. At $T > T_c$, where $s = 0$, it follows from (18) that

$$\varepsilon = \varepsilon_0 + \frac{ce(q - 1)}{q(Tq - Ic)} \tag{19}$$

and ε when $T \to T_0 = Ic/q \sim T_c$ suddenly increases. Below T_c, ε suddenly decreases and $\Delta\varepsilon = \varepsilon(T_c, s = 0) - \varepsilon(T_c, s_c)$.

3. Results and Discussion

The dielectric constant ε has been measured by the method described previously [18] in the temperature range from 4.2 to 300 K at a frequency of 10^3 Hz using powder samples of the clathrates $Q_\beta \cdot CH_3OH$ ($c = 0.99$), and $Q_\beta \cdot SO_2$ ($c \approx 0.9$). The sample was placed in a glass ampoule. Before the beginning of the experiment, the powder was slightly pressed and, afterwards, the loading was removed. The results of the $\varepsilon(T)$ measurements are shown in Figure 1.

In $Q_\beta \cdot CH_3OH$, when the temperature of the sample decreased from 300 to 4.2 K, $\varepsilon(T)$ increases near the points $T_{c1}^{decr} \approx 230$ K and $T_{c2}^{decr} \approx 48$ K. The jump of the dielectric constant at T_{c1} is equal $\Delta\varepsilon/\varepsilon \approx 9\%$ and at T_{c2} is $\Delta\varepsilon/\varepsilon \approx 19\%$. When the temperature of the sample increases from 4.2 K, the temperature points where $\varepsilon(T)$ is a maximum differ noticeably from the values obtained with decreasing temperature (Figure 1a).

In $Q_\beta \cdot SO_2$, anomalies in $\varepsilon(T)$ can also be observed at two points (Figure 1b) but the values of the heat-capacity lags, $\Delta T_1 = T_{c1}^{incr} - T_{c1}^{decr} \approx 9°$ and $\Delta T_2 = T_{c2}^{incr} - T_{c2}^{decr} \approx 13°$, are smaller than in Q_β with methanol. Thus, our results show that, in hydroquinone clathrates, at the points T_{c1} and T_{c2}, the PT's to ferroelectric or anti-ferroelectric states occur [19].

$Q_\beta \cdot CH_3OH$. In this compound, $\varepsilon(T)$ has been measured by various authors (see, e.g., [14, 15] and literature cited therein). All these results show that $\varepsilon(T)$ increases anomalously in the region $T \to T_c \approx 70$ K. The maximum values of $\varepsilon_{max}(T_c)$ obtained by various authors on monocrystals and on powder samples strongly differ ($\varepsilon_{max} = 5.5$–180 [14]).

Two significant new results follow from our measurements: $\varepsilon(T)$ increases at the T_{c2} region and large heat-capacity lags ΔT_1, and ΔT_2 are observed. The reasons for the increase in $\varepsilon(T)$ at $T \to T_{c1}$ are not obvious without additional experiments. However, it is possible that the PT at $T \to T_{c1}$ is related with the proton subsystem reconstruction in the Q_β lattice or with the change of concentration c. Quite different reasons are responsible for the PT at T_{c2} point. Here, orientational ordering of the methanol molecules in the cavities takes place. Using the value of $q = 6$ for CH_3OH [15] we can see that the theory developed in the former section adequately describes (in a qualitative sense) the experimental data obtained, i.e., the first order
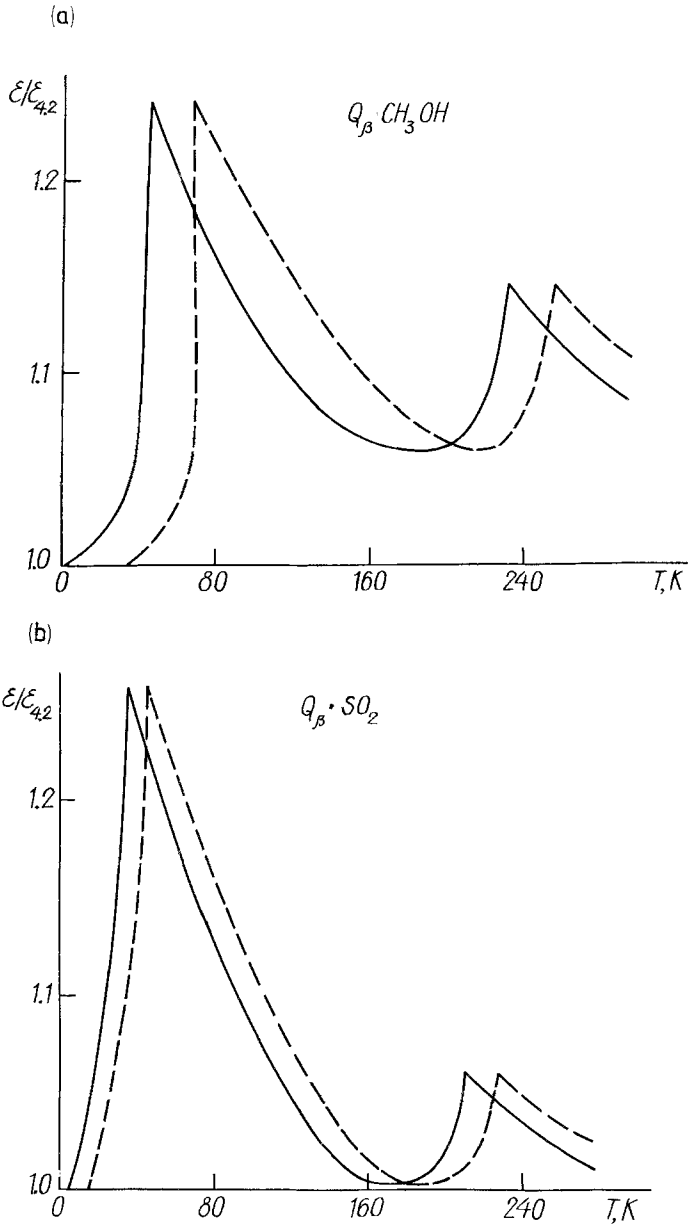
(a)

(b)

Fig. 1. Temperature dependence of the dielectric constant $\varepsilon(T)/\varepsilon(T = 4.2 \text{ K})$ in hydroquinone clathrates. The solid lines were obtained with decreasing temperature, the dashed lines with increasing temperature.

PT ($\Delta T_2 \neq 0$), the anomalous increase of $\varepsilon(T)$ at $T \to T_{c2}$ and the jump of $\Delta\varepsilon(T_{c2})$. We can also make some quantitative calculations. Inserting $T_c = 68$ K and $q = 6$ into (14) we obtain $I = 276$ K. On the other hand, in agreement with [7], $w = v + (q - 1/q)I = -1787$ K. Then $v = -2017$ K. The value $\varepsilon_{\text{max}}(T)$ is calculated from (19) taking $p = 1.7$ D and $V_c \approx 510$ Å. Thus, $\varepsilon_{\text{max}} \approx 75$, which coincides with the data obtained for monocrystals [14]. When $\varepsilon^{-1}(T) \to 0$, the temperature T_0 equals 45 K and the order parameter jump $s_c = 0.8$.

$Q_\beta \cdot SO_2$. As we know, there were no data about the PT in this compound. Our theory and the results of our experiment allow us to draw the following conclusions. The value of ΔT_2 is smaller in $Q_\beta \cdot SO_2$ than in $Q_\beta \cdot CH_3OH$. Thus, very likely, the jump of $s_c(T_c) < 0.8$. This means that the SO_2 molecule is orientated among $q < 6$ equilibrium states. We assumed that $q = 4$. Then, inserting $T_c = 44$ K into (14) we obtain $I = 161$ K. Using region II in [7], $v = -320$ K. This shows that the compensation effects among the interactions v_{11}, v_{12}, and v_{22} are much stronger in $Q_\beta \cdot SO_2$ than in $Q_\beta \cdot CH_3OH$. Then, taking $p = 1.7$ D we obtain from (19) that $\varepsilon_{max} \approx 290$ and $T_0 = 36$ K.

The comparison shows that the theory proposed explains qualitatively the experimental data obtained.

Acknowledgements

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