

The Vibrational Energy of H₂S

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TABLE I.

	<i>E</i>	2 <i>C</i> ₂	3 <i>C</i> ₂	3σ _h	4 <i>T</i>	9σ _g	2 <i>T</i> ₂	6 <i>S</i> ₂	6 <i>T</i> ₂	<i>n</i> _i	<i>n</i> _i '	Raman	Infra-red
<i>A</i> ₁	1	1	1	1	1	1	1	1	1	3	3	<i>P</i>	<i>P</i>
<i>A</i> ₂	1	1	1	1	1	1	1	1	1	1	1	<i>f</i>	<i>f</i>
<i>A</i> ₃	1	1	1	1	1	1	1	1	1	1	1	<i>f</i>	<i>f</i>
<i>A</i> ₄	1	1	1	1	1	1	1	1	1	1	1	<i>f</i>	<i>f</i>
<i>E</i> ₁	2	2	2	0	1	0	1	0	1	0	0	<i>f</i>	<i>f</i>
<i>E</i> ₂	2	2	2	0	1	0	1	0	1	0	0	<i>f</i>	<i>f</i>
<i>E</i> ₃	2	2	2	0	1	0	1	0	1	0	0	<i>f</i>	<i>f</i>
<i>E</i> ₄	2	2	2	0	1	0	1	0	1	0	0	<i>f</i>	<i>f</i>
<i>G</i>	4	4	4	0	1	0	1	0	1	0	0	<i>P</i>	<i>P</i>
	24	0	0	0	48	36	0	0	0				
	18	0	0	0	36	36	0	0	12				
	12	0	12	12	24	36	0	24	24				
	6	0	0	0	12	18	0	0	0				

taken into account. However, in some molecules, it may be possible to consider other elements of symmetry, as for example, a twist through 120° of one of the CH₃ groups against the other in the molecule C₂H₆. Using the point group *D*_{3h} Howard† obtained the normal modes, etc., of this molecule. In this paper, assuming that the potential energy has the symmetry of the molecule including the twist also, the symmetry characters of the modes and the selection rules for their appearance in the Raman effect and the infra-red absorption are given. The results are tabulated in Table I. Details regarding the normal frequencies will be published separately.

† J. B. Howard, J. Chem. Phys. 5, 442 (1937).

The Vibrational Energy of H₂S*

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August 1, 1950

THE approximate location of four new band centers in the infra-red spectrum of hydrogen sulfide has enabled the evaluation of the complete quadratic expression for the unperturbed vibrational energies as

$$(E - E_0) \text{ cm}^{-1} = 2651n_\sigma + 2635n_\pi + 1189n_\delta - 26n_\sigma^2 - 24n_\pi^2 - 6n_\delta^2 - 90n_\sigma n_\pi - 19n_\sigma n_\delta - 20n_\pi n_\delta. \quad (1)$$

Equation (1) yields the unperturbed levels shown in column 2 of Table I. From the observed perpendicular type bands^{1,2} at 9911 cm⁻¹ and 10194 cm⁻¹, the Darling-Dennison³ parameter γ may be evaluated as 47 cm⁻¹. The calculated energy values for the two pairs of interacting levels are listed in column 3 of the table.

The constants in (1) and the Darling-Dennison interaction parameter were evaluated from the unstarred levels in Table I.

TABLE I.

<i>n</i> _σ	<i>n</i> _π	<i>n</i> _δ	Unperturbed	DD resonance
0	0	1	1183 ⁷	
0	0	2	2354 ⁷	
0	1	0	2611 ⁴	
1	0	0	2625 ⁴	
1	0	1	3789 ⁷	
1	1	0	5146 ⁷	
0	2	0	{5174}	*5138 ⁷
2	0	0	{5198}	*5234 ⁸
1	1	1	6290 ⁶	
2	2	0	*10012 ⁸	
1	3	0	{10044}	9911 ¹
3	1	0	{10060}	10194 ²
0	4	0	*10156 ⁸	
4	0	0	10188 ²	

The absorption in the region⁹ of 5146 cm⁻¹ shows an overlapping spectrum centered at approximately 5143 cm⁻¹ as compared to the calculated value 5138 cm⁻¹ for the perturbed (020) band. The appearance of this parallel type band is presumably due to the borrowing of intensity through rotational interaction from the neighboring (110) perpendicular type band just as has been previously indicated in the appearance of the (400) band² at 10188 cm⁻¹.

The analysis of the 8μ-region reveals that recent investigators have not detected the *P* branch.¹⁰⁻¹² The early investigation of Mischke,¹³ however, shows a weak *P* branch extending from 1180 cm⁻¹ to nearly 1000 cm⁻¹.

As would reasonably be expected the results described by (1) are analogous to a similar treatment of the water vapor system.³ The most conspicuous feature of this analysis is the low frequency of the bending fundamental, from 50 to 100 cm⁻¹ less than it has recently been considered to be.¹⁴

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⁴ G. M. Murphy and J. E. Vance, J. Chem. Phys. 6, 426 (1938).

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⁷ To be reported shortly.

⁸ Not yet observed.

⁹ Unpublished data of M. K. Wilson.

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¹³ W. Mischke, Zeits. f. Physik 67, 106 (1931).

¹⁴ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 283.

The Quantum-Mechanical Equation of State

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IN the last few years there has been some disagreement about the equivalence of the thermodynamic and kinetic pressure of a quantum liquid, with special emphasis on liquid helium II. The kinetic pressure is obtained from the quantum-mechanical virial theorem. Equations of state which do not appear to be identical have been derived from statistical thermodynamics by H. S. Green¹ and J. de Boer.² In this note, a simple derivation will be given, which may expose more clearly the assumptions required.

By differentiating the partition function with respect to volume, we get

$$-p = \frac{\partial A}{\partial v} = \sum_i e^{\beta(A-E_i)} \frac{\partial E_i}{\partial v} \quad (1)$$

where all symbols have their usual significance. The dependence of the energy levels of the system on its volume is needed. To get this, we introduce a scale factor, depending on the volume, into the Schrödinger equation for the system, and determine the dependence of the energy levels on this scale factor. This device is related to the one used by H. S. Green to get the classical equation of state, and by de Boer for the quantum-mechanical case. The Hamiltonian operator for the system is

$$H = -\frac{\hbar^2}{2m} \sum_{k=1}^N \nabla_{\mathbf{r}_k}^2 + V(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (2)$$

The potential is assumed to become infinite at the walls. This wall potential is taken into account by requiring eigenfunctions to vanish at the walls. We define a new coordinate system,

$$\mathbf{r}_k = v^{1/3} \mathbf{R}_k \quad (3)$$

where *v* is the volume of the system. A variation in *v* corresponds to an expansion or contraction of the system, without any change in its relative shape or configuration. The equation of state that will result will be valid only for such changes in volume. However, when the dimensions of the system are large compared with the

mean de Broglie wave-length of a particle, one may expect that its thermodynamic properties will not depend on its shape. Keeping R_k fixed, and varying v , the Hamiltonian becomes an explicit function of the volume:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(v^1 R_{11} \cdots v^N R_N). \quad (4)$$

By differentiating the Schrödinger equation with respect to v , at constant R_k ,

$$\frac{\partial H \psi_i}{\partial v} = H \frac{\partial \psi_i}{\partial v} + \frac{\partial H}{\partial v} \psi_i = \frac{\partial E_i \psi_i}{\partial v} = E_i \frac{\partial \psi_i}{\partial v} + \frac{\partial E_i}{\partial v} \psi_i. \quad (5)$$

Multiply through by ψ_i^* and integrate over configuration space,

$$\frac{\partial E_i}{\partial v} = \int \psi_i^* \frac{\partial H}{\partial v} \psi_i d\tau + \int \psi_i^* (H - E_i) \frac{\partial \psi_i}{\partial v} d\tau. \quad (6)$$

Because of its Hermitian character, the latter term vanishes, and

$$\frac{\partial E_i}{\partial v} = \int \psi_i^* \frac{\partial H}{\partial v} \psi_i d\tau \quad (7)$$

—a not unexpected result. Put this into Eq. (1), and make use of the following property of the statistical operator,

$$\exp(\beta(A - H)) \psi_i = \exp(\beta(A - E_i)) \psi_i \quad (8)$$

to get

$$-p = \sum_i \exp(\beta(A - E_i)) \frac{\partial E_i}{\partial v} = \sum_i \int \psi_i^* \frac{\partial H}{\partial v} \exp(\beta(A - H)) \psi_i d\tau. \quad (9)$$

An important feature of this is that there is no difficulty here with the commutivity of the operators. This has been a source of confusion in the treatments of Green and de Boer. By carrying out the differentiation of the Hamiltonian, as de Boer has shown, the result is

$$pv = \frac{2}{3} \sum_{k=1}^N \left\langle \frac{P_k^2}{2m} \right\rangle - \frac{1}{3} \sum_{k=1}^N \langle \mathbf{r}_k \cdot \nabla \mathbf{r}_k V \rangle \quad (10)$$

where averages are taken over the canonical ensemble. (P_k is now the momentum operator.)

The final equation obtained by de Boer differs from this in that he uses an expansion of the energy eigenfunctions in free particle wave functions. This is justified, since the energy eigenfunctions correspond to a bound state, are quadratically integrable, and may be expressed as Fourier transforms.

This equation of state is identical with that obtained from the virial theorem, so that the kinetic and thermodynamic pressures are the same for a quantum fluid.

* Contribution No. 1441.

¹ H. S. Green, in Born and Green, *A General Kinetic Theory of Liquids* (Cambridge University Press, 1949) p. 23; *Physica* 15, 882 (1949).

² J. de Boer, Reports on Progress in Physics XII, pp. 325–335; *Physica* 15, 843 (1949).

Dissolution of Phenanthrene in Compressed Gases

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July 31, 1950

THE apparatus employed for the compression of argon and nitrogen has already been described.¹

Our concentration measurement rests on Beer's law, of which the validity at the very low concentration of our solutions is unquestionable. But the optical density of a given band does not give directly the variation of the concentration with pressure, as one must take into account some specific effects of pressure and temperature on the intensity and position of the band. Those effects are given by the investigation of unsaturated solutions, where the concentration in g/cm³ is constant;² temperature and pressure are varied in such a way that the gas can never get out of the bomb for the duration of the experiment.

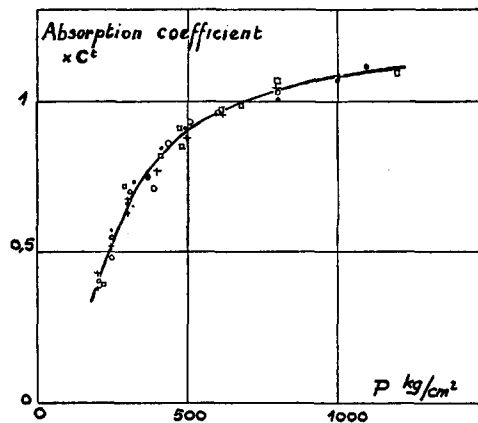


FIG. 1. Absorption coefficient times c^t versus pressure.

Figure 1 shows that the specific effect of pressure is relatively important. On the other hand, between 0°C and 50°C, no measurable specific effect of temperature could be found.

The method used does not give the solubility in absolute value; this value is supplied approximately by the measure of the mass of phenanthrene used to make unsaturated solutions, and also by comparison with the spectrum of a solution in cyclohexane of known concentration; thus we evaluated to 10^{-6} g/cm³ the mass of phenanthrene contained in 1 cm³ of saturated solution in compressed nitrogen at 600 kg/cm² and 17°C.

Figure 2 represents the decimal logarithm of the mass m of phenanthrene dissolved in 1 cm³ of compressed gas as a function of the density of the gas. It can be seen that:

$$m = C \exp^n e^{\alpha p} \quad (1)$$

at constant temperature.³ The measurements are not accurate enough for the exact determination of n ; but they show nevertheless that n is certainly small. The curves in Fig. 3 show that:

$$m = A e^{-B/T} \quad (2)$$

at constant density⁴ where B is a constant which depends on the

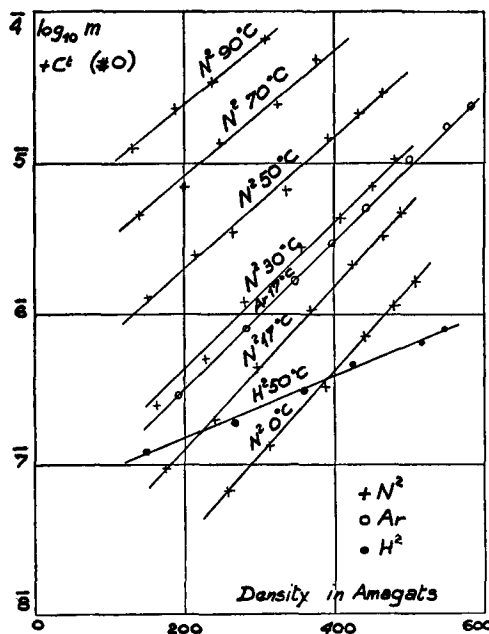


FIG. 2. $\log_{10} m - c^t$ versus density for N_2 , Ar and H_2 .