within this range. The grain size of samples compressed from 10 000 to 200 000 lb/in.[2] appears to lie between 5×10^{-3} and 2×10^{-4} mm.

The finding that the respective Debye rings in the diffraction patterns remained the same distance from the undeviated x-ray beam for all of the compressed samples, indicated no change in crystal lattice structure as a result of the applied pressure. It appears that although these translucent compressed crystal samples resembled in appearance single crystals, they retained x-ray diffraction patterns characteristic of powder crystals. It may be that crystals prepared in this way can be used as phosphors in scintillation counters.

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[1] J. G. Kereiakes, dissertation, University of Cincinnati, 1950 (unpublished).

[2] M. A. Ford and G. R. Wilkinson, J. Sci. Instr. **31**, 338 (1954).

[3] W. T. Sproull, *X-Rays in Practice* (McGraw-Hill Book Company, Inc., New York, 1946), p. 440.

Infrared Absorption of Liquid and Solid Hydrogen*

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The fundamental vibrational absorption of hydrogen, induced by intermolecular forces, has been studied over a wide range of gas pressures and at temperatures down to 80°K.[1–4] The resolution of the components of the band improves greatly as the temperature is lowered; for this reason, as well as to ascertain the effect of crystal structure on induced absorption, the investigation has been extended to liquid and solid hydrogen.

A fused quartz absorption cell, giving a path length of 8.4 mm, was suspended in a cryostat of special design. Temperatures in the range 10–22°K were maintained constant to ±0.1°K by controlling the boiling of liquid helium below the cell with a heating coil, and were measured by the vapor pressure of the hydrogen in the cell. A Perkin-Elmer 12B spectrometer with a LiF prism and a PbS detector was used. Figure 1 shows the fundamental absorption of liquid normal hydrogen at 18°K and of the solid at 11°K, along with the absorption of the compressed gas at 298°K with approximately the same density.

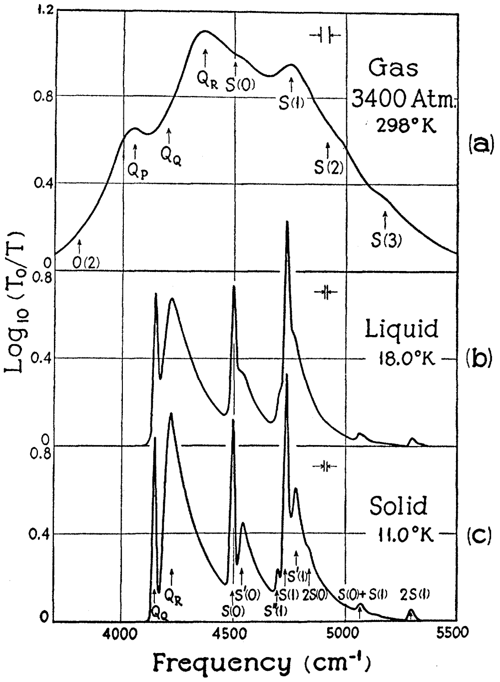

Fig. 1. The fundamental infrared absorption of hydrogen induced by intermolecular forces for (a) the compressed gas at a density of 1014 Amagat units, (b) the liquid at 817 Amagat, and (c) the solid at 972 Amagat.

Several features of the absorption of the compressed gas are now well established. The Q_Q component [not well resolved under the experimental conditions of Fig. 1(a)] and various rotational lines with $\Delta J=\pm2$, of which $S(0)$ and $S(1)$ are the most prominent, have frequencies near those calculated for the free molecule at all gas densities; the intensity of these components is believed to arise chiefly from the quadrupole interactions between the absorbing molecule and the surrounding molecules.[5] The maxima Q_P and Q_R, on the other hand, change markedly with the density and the temperature; their separations from the band origin increase with increasing density and temperature, and the intensity of Q_P diminishes rapidly as the temperature is lowered. These components of the Q branch probably originate in close collisions in the region of overlap forces, and the relative kinetic energy of the surrounding molecules can apparently participate in the absorption process.[3]

In the spectrum of the solid, the sharp lines Q_Q, $S(0)$, and $S(1)$ in Fig. 1(c), can be ascribed to the quadrupole field effect. Confirmation of this view has been furnished by preliminary experiments on pure parahydrogen in which the disappearance of Q_Q, in accordance with the vanishing of the matrix element for the transition $J=0$ to $J'=0$,[5] has been established. Certain minor maxima can be identified from their frequencies as the double rotational transitions $2S(0)$, $S(0)+S(1)$, and $2S(1)$; in parahydrogen $2S(0)$ appears alone, as a sharp line with medium intensity. The weak maximum, $S''(1)$, belongs to the $S(1)$ group, but its origin is not clear.

The higher-frequency components of the S lines, labelled $S'(0)$ and $S'(1)$ in Fig. 1(c), have contours very similar to Q_R and are accordingly ascribed to overlap forces. The interaction with the kinetic energy of the surrounding molecules in the gas must here become an interaction with the vibrational energy of the crystal lattice. The splitting off of the components, $S'(0)$ and $S'(1)$, is first noticeable at about 20°K and is more or less complete at 15°K; there is no change observed on passing the solidification point at 14°K, and very little on lowering the temperature to 4.2°K, the boiling point of liquid helium. If the characteristic appearance of the spectrum of the solid is due to the participation of the lattice modes in the absorption, it is clear that the crystalline structure persists locally into the liquid state several degrees above the fusion point.

Induced infrared absorption is caused by the *asymmetric* distortion of the absorbing molecule by intermolecular forces. In crystalline hydrogen asymmetric distortion can be produced both by the random orientations of the freely rotating molecules and by the vibrational motion of the crystal lattice. The experimental results indicate that the first type of distortion occurs for quadrupole interactions, and that both types are operative for overlap interactions.

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[†] Holder of a research fellowship of the National Research Council of Canada.

[‡] Holder of a scholarship of the Research Council of Ontario.

[1] Welsh, Crawford, and Locke, Phys. Rev. **76**, 580 (1949).

[2] Chisholm, McDonald, Crawford, and Welsh, Phys. Rev. **88**, 957 (1952).

[3] D. A. Chisholm and H. L. Welsh, Can. J. Phys. **32**, 391 (1954).

[4] Chisholm, Hare, and Welsh, J. phys. radium **15**, 511 (1954).

[5] J. van Kranendonk, dissertation, Amsterdam, 1952 (unpublished); J. van Kranendonk and R. Bird, Physica **17**, 153 (1952).

Canonical Invariance in Lagrangian Quantum Mechanics

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HUGENHOLTZ,[1] in a recent Letter to the Editor, has criticized Schwinger's[2] variational formalism in quantum mechanics by attempting to show that it is possible, by means of a unitary transformation on the dynamical variables, to add terms to the Lagrange function which are not in the form of time derivatives. He gives as an example $L''=-\frac{1}{2}(q^2\dot{q}+\dot{q}q^2)$ which arises from $U=\exp(\frac{1}{3}iq^3)$ and concludes that the new Lagrange function $L'=L+L''$ is 'essentially different' from the old one L.

This is not the case; the condition for canonical invariance is that the *variation* of the added term[2] rather than the added term itself should be a time derivative. If we evaluate $\delta L''$ we find

$$\begin{aligned}\delta L'' &= -\tfrac{1}{2}(\delta q q\dot{q}+q\delta q\dot{q}+q^2\delta\dot{q}+\delta\dot{q}q^2+\dot{q}\delta q q+\dot{q}q\delta q)\\ &= -(q\dot{q}+\dot{q}q)\delta q+\frac{d}{dt}(q^2)\cdot\delta q-\frac{d}{dt}(q^2\delta q) \qquad (1)\\ &= -\frac{d}{dt}(q^2\delta q)=\frac{d}{dt}\delta(-\tfrac{1}{3}q^3),\end{aligned}$$

where we have used the commutativity of q with all its coefficients. Thus the new Lagrange function is equivalent to the old one.

The effect of making a general unitary transformation, not explicitly dependent on the time, can be seen as follows. First, every unitary transformation U can be written

$$U=\exp(iG), \tag{2}$$

where G is Hermitian. Secondly, a unitary transformation of the dynamical variables at a time intermediate between the initial and final times has no effect on the transformation function:

$$\begin{aligned}&(\alpha_1't_1|\alpha_2''t_2)\\ &=\int(\alpha_1't_1|\alpha't)d\alpha'(\alpha't|\alpha_2''t_2),\quad t_1>t>t_2\\ &\to\int(\alpha_1't_1|U(t)|\alpha't)d\alpha'(\alpha't|U^{-1}(t)|\alpha_2''t_2) \qquad (3)\\ &=(\alpha_1't_1|\alpha_2''t_2).\end{aligned}$$

This shows that (2) induces

$$(\alpha_1't_1|\alpha_2''t_2)\to(\alpha_1't_1|U^{-1}(t_1)U(t_2)|\alpha_2''t_2). \tag{4}$$

Since the only change is at the times t_1 and t_2, Schwinger's operator form of Hamilton's principle is left unaffected. Thus if an admissible variation be made, the contribution to the variation of the transformation function arising from U is

$$-i(\alpha_1't_1|U^{-1}(t_1)[\delta G(t_1)-\delta G(t_2)]U(t_2)|\alpha_2''t_2).$$

But the same effect would be produced if we added $-(d/dt)\delta G$ to δL, since $\int dt(d/dt)\delta G=\delta G(t_1)-\delta G(t_2)$. Hence U induces

$$\delta L\to\delta L-(d/dt)\delta G. \tag{5}$$

Hugenholtz's final point that c-number variations do not transform into c-number variations under arbitrary unitary transformations does not seem relevant. The point is more whether *admissible* variations transform into *admissible* variations. In all the cases which have been studied so far,[2] it can be seen that a variation consisting of the sum of two nonvanishing parts, one of which commutes and the other of which anticom-