Second-Harmonic Generation of Light at the Boundary of an Isotropic Medium

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Measurements of second-harmonic generation of light from liquid-air interfaces are reported. A physical model is proposed in which the observed harmonics arise from the electric double layer at the surface. The experimental results from the surfaces of various liquids and solids are discussed in the light of this model.

INTRODUCTION

THIS paper presents the first measurements of second-harmonic generation of light at several liquid-air interfaces, and discusses the phenomenology of second-harmonic generation at the surface of an isotropic medium. The second-harmonic wave radiated from the boundary is described in terms of an effective nonlinear surface polarization with three nonzero independent coefficients. A physical model is proposed in which the observed harmonics arise from the electric double layer at the surface. The nonlinear coefficients deduced for various liquids and solids are discussed in the light of this model.

NONLINEAR SURFACE POLARIZATION

Consider the surface of an isotropic medium placed in vacuum. There exists near the surface a transition region over which the dielectric constant changes rapidly from unity to its value in the bulk. It will be assumed that, with a light wave incident onto the boundary of the medium, the second-harmonic radiation generated in the transition region can be characterized by a nonlinear polarization proportional to the square of the electric field just outside the region. Here we have neglected the possible dependence of this polarization on the propagation vector of the linear fields outside the region. As the various components of these linear fields are related linearly, the field inside the medium will be used in the following discussion. General symmetry considerations show that within the transition region the contribution to the nonlinear polarization at the second-harmonic frequency may be given phenomenologically as follows:

$$P_i^S(2\omega)=(A-B)[n_jE_j(\omega)]^2n_i+Bn_jE_j(\omega)E_i(\omega)+CE_j(\omega)E_j(\omega)n_i. \quad (1)$$

Here $\mathbf{n}$ is a unit vector normal to the surface; A, B, and C are three constants; and $E_j(\omega)$ is the jth component of the electric-field amplitude at the fundamental frequency ω inside the medium. This surface polarization radiates into the media on either side of the surface, giving rise to the observed second-harmonic waves. It includes the effect due to local-field corrections within the transition region as well as the contribution arising from higher-order multipole polarizations; and, as such, it is defined as the *effective* total nonlinear surface polarization per unit area of the surface. It can be shown by explicit calculation that, with the transition region thin compared to the wavelength, the resulting radiation field is independent of the exact location of this *effective* nonlinear polarization near the boundary of the medium. To facilitate comparison with previously published results,[1,2] a new set of three constants $\alpha_{\rm eff}$, $\beta_{\rm eff}$, and $\gamma_{\rm eff}$ will be introduced: $A=\frac{1}{2}(\epsilon_S^2-1)\alpha_{\rm eff}$, $B=(\epsilon_S-1)\beta_{\rm eff}$, $C=\gamma_{\rm eff}/2\epsilon_T$; and ϵ_S and ϵ_T are the dielectric constant of the medium at the fundamental frequency ω and the second-harmonic frequency 2ω, respectively. In terms of these new coefficients, the components of the nonlinear surface polarization normal and tangential to the surface are given, respectively, as follows:

$$P_z^S(2\omega)=\tfrac{1}{2}(\epsilon_S^2-1)\alpha_{\rm eff}E_z^2(\omega)+(\gamma_{\rm eff}/2\epsilon_T)E^2(\omega), \quad (2)$$

$$P_{x,y}^S(2\omega)=(\epsilon_S-1)\beta_{\rm eff}E_z(\omega)E_{x,y}(\omega). \quad (3)$$

Consider now a light wave with frequency ω incident from the vacuum onto the boundary of an isotropic medium occupying the half-space $z\leq 0$. The amplitude of the incident light wave is given by

$$\mathbf{E}_0(\mathbf{r},t)=\mathbf{E}_0\exp[i(-k_0z\cos\theta_i+k_0x\sin\theta_i)-i\omega t]+\text{c.c.}, \quad (4)$$

where $\mathbf{E}_0=(E_0\cos\theta_i\cos\varphi,\ E_0\sin\varphi,\ E_0\sin\theta_i\cos\varphi)$; $k_0=\omega/c$, c being the velocity of light in vacuum; θ_i is the angle of incidence in the plane $y=0$, and φ is the angle between $\mathbf{E}_0$ and the plane of incidence. With this field incident, the second-harmonic waves reflected and transmitted from the boundary are of the form

$$\mathbf{E}^R(\mathbf{r},t)=\mathbf{E}^R(2\omega)\exp[i2k_0(z\cos\theta_i+x\sin\theta_i)-i2\omega t]+\text{c.c.} \quad (5)$$

and

$$\mathbf{E}^T(\mathbf{r},t)=\mathbf{E}^T(2\omega)\exp[i2k_0\epsilon_T^{1/2}(-z\cos\theta_T+x\sin\theta_T)-i2\omega t]+\text{c.c.}, \quad (6)$$

respectively. Here, $\sin\theta_i=\epsilon_S^{1/2}\sin\theta_S=\epsilon_T^{1/2}\sin\theta_T$. The

[1] C. C. Wang and A. N. Duminski, Phys. Rev. Letters **20**, 668 (1968); **21**, 266(E) (1968), and references therein.

[2] N. Bloembergen, R. K. Chang, S. S. Jha, and C. H. Lee, Phys. Rev. **174**, 813 (1968). The author is indebted to Professor Bloembergen for sending him a copy of their paper prior to publication. The new set of coefficients $\alpha_{\rm eff}$, $\beta_{\rm eff}$, and $\gamma_{\rm eff}$ may be compared to the set of coefficients α, β, and 2γ in Ref. 1, and to the set of coefficients δ, $\bar{\beta}$, and 2γ in Ref. 2. However, as will become clear later in this paper, this new set of coefficients represent the *measured* quantities which include both surface and volume nonlinearities, whereas the sets of coefficients in Refs. 1 and 2 are defined as the coefficients for the bulk quadrupolar nonlinearities only.

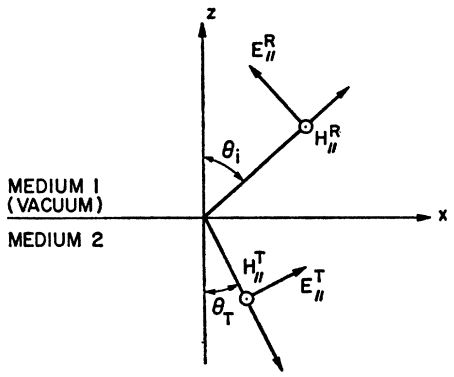

FIG. 1. Schematic showing the reflected and transmitted second-harmonic waves at the boundary of an isotropic medium.

amplitudes $\mathbf{E}^R(2\omega)$ and $\mathbf{E}^T(2\omega)$ can be determined by direct integration of the effective nonlinear polarization over the entire area of the surface, or by imposing the following set of boundary conditions appropriate for the various components of the nonlinear surface polarization. In the following, we shall use the boundary conditions to calculate the radiation field due to each component of the effective polarization separately, and obtain the total field $\mathbf{E}^R(2\omega)$ by adding these various contributions. The method of direct integration is straightforward but tedious, giving the same results.

First, for the normal component $P_z^S(2\omega)$, the tangential component of the resulting magnetic field at the harmonic frequency is continuous (Fig. 1), but the tangential component of the electric field $E_{\parallel}(2\omega,z)$ is discontinuous[3]:

$$E_{\parallel}^R(2\omega,z)=\epsilon_T^{1/2}E_{\parallel}^T(2\omega,z), \tag{7}$$

$$E_{\parallel}^R(2\omega,z)\cos\theta_i+E_{\parallel}^T(2\omega,z)\cos\theta_T = 4\pi[\delta P_z^S(2\omega)/\delta x]. \tag{8}$$

For the components $P_x^S(2\omega)$ and $P_y^S(2\omega)$, the tangential components of the resulting electric field $E_{\parallel}(2\omega,x)$ and $E_{\perp}(2\omega,y)$ are always continuous, but the tangential components of the resulting magnetic field are discontinuous and are related, respectively, to $-i(8\pi\omega/c)P_x^S(2\omega)$ and $-i(8\pi\omega/c)P_y^S(2\omega)$ in the usual manner:

$$E_{\parallel}^R(2\omega,x)\cos\theta_i=-E_{\parallel}^T(2\omega,x)\cos\theta_T, \tag{9}$$

$$E_{\parallel}^R(2\omega,x)-\epsilon_T^{1/2}E_{\parallel}^T(2\omega,x)=-i(8\pi\omega/c)P_x^S(2\omega), \tag{10}$$

$$E_{\perp}^R(2\omega,y)=E_{\perp}^T(2\omega,y), \tag{11}$$

$$E_{\perp}^R(2\omega,y)\cos\theta_i+\epsilon_T^{1/2}E_{\perp}^T(2\omega,y)\cos\theta_T = -i(8\pi\omega/c)P_y^S(2\omega). \tag{12}$$

Combining Eqs. (7)–(12), one obtains the following expressions for the components $E_{\parallel}(2\omega)$ and $E_{\perp}(2\omega)$ of the total field $\mathbf{E}^R(2\omega)$ parallel and perpendicular to the plane of incidence[4,5]

$$E_{\parallel}^R(2\omega)=(32\pi\omega/c)E_0^2\sin\theta_i\cos^2\theta_i\cos^2\varphi[1/\epsilon_S^{1/2}g_{OS}^2g_{OT}] \times\{\tfrac{1}{2}[\epsilon_T(\epsilon_S^2-1)\alpha_{\rm eff}\sin^2\theta_i +\epsilon_S\gamma_{\rm eff}(1+g_{OS}^2g_{IS}^{-2}\tan^2\varphi)](\epsilon_S\epsilon_T)^{-1/2} -\beta_{\rm eff}(\epsilon_S-1)\cos\theta_S\cos\theta_T\}, \tag{13}$$

$$E_{\perp}^R(2\omega)=(32\pi\omega/c)E_0^2\sin\theta_i\cos^2\theta_i\sin\varphi\cos\varphi \times[(\epsilon_S-1)\beta_{\rm eff}/\epsilon_S^{1/2}g_{IS}g_{OS}g_{IT}], \tag{14}$$

where

$$g_{OS}=\epsilon_S^{1/2}\cos\theta_i+\cos\theta_S, \tag{15}$$

$$g_{IS}=\epsilon_S^{1/2}\cos\theta_S+\cos\theta_i, \tag{16}$$

$$g_{OT}=\epsilon_T^{1/2}\cos\theta_i+\cos\theta_T, \tag{17}$$

$$g_{IT}=\epsilon_T^{1/2}\cos\theta_T+\cos\theta_i. \tag{18}$$

NONLINEAR POLARIZATION IN THE BULK

In an isotropic medium, the lowest-order contribution to the nonlinear polarization at the second-harmonic frequency may be given phenomenologically as follows:

$$P_i(2\omega)=(\alpha-\beta-2\gamma)E_j(\omega)\nabla_jE_i(\omega) +\beta E_i(\omega)\nabla_jE_j(\omega)+2\gamma E_j(\omega)\nabla_iE_j(\omega), \tag{19}$$

where α, β, and γ are three constants. Equation (19) can be written so that the terms are either symmetric or antisymmetric in the last two indices:

$$P_i(2\omega)=\tfrac{1}{2}(\alpha-\beta)E_j(\omega)[\nabla_iE_j(\omega)+\nabla_jE_i(\omega)] +\beta E_i(\omega)\nabla_jE_j(\omega)+[2\gamma-\tfrac{1}{2}(\alpha-\beta)] \times E_j(\omega)[\nabla_iE_j(\omega)-\nabla_jE_i(\omega)]. \tag{20}$$

Here the first two terms, which are symmetric in the last two indices, describe the electric quadrupole nonlinearity[6]; the last term, which is antisymmetric in the last two indices, describes the magnetic dipole nonlinearity referred to previously as the Lorentz force term.[7]

For a transverse electromagnetic wave, the first two terms in Eq. (19) are zero in the bulk; the last term gives rise to a longitudinal polarization, and so it is observable only in experiments involving a discontinuity, such as the boundary of a medium. The radiation field resulting from this magnetic dipole term has

[3] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Co., New York, 1941), p. 191.

[4] Equations (13) and (14) may also be obtained by using the method of Bloembergen and Pershan in Ref. 8 and assuming that the "effective dielectric constant" ϵ_M defined there is unity for the surface layer. Thus, by reinstating a multiplying factor of $(\epsilon_T/\epsilon_M)(\epsilon_S+1)/2$ for the α term in Eq. (4) of Ref. 1, one obtains with $\epsilon_M=1$ the same result as Eq. (13).

[5] In Ref. 2, Bloembergen *et al.* have obtained the same result from their Eq. (37). They find, however, that this result differs in angular dependence from that obtained from their Eq. (35), which in turn is based on a boundary condition stated as their Eq. (25). Ironically, this boundary condition is not correct, as it ignores the fact that the normal component of the electric field behaves as a δ function inside the surface double layer.

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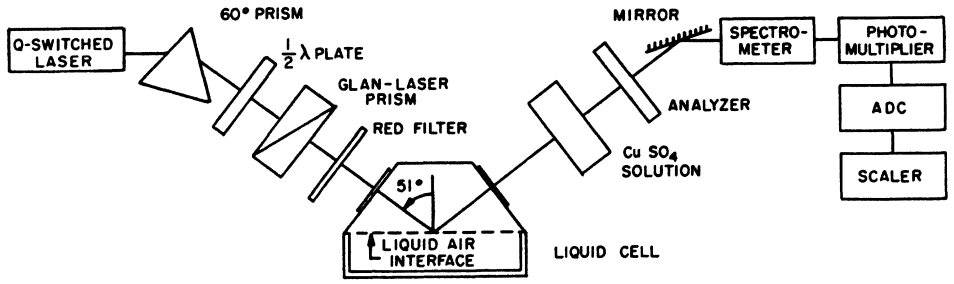

FIG. 2. Schematic of the experimental arrangement.

been calculated previously,[8] and is given by

$$E_{11}^{R}(2\omega)=(32\pi\omega/c)E_0^2\sin\theta_i\cos^2\theta_i\cos^2\varphi[1/\epsilon_S^{1/2}g_{0T}g_{0S}^2]\times[-\gamma(\epsilon_S/\epsilon_T)^{1/2}(1+g_{0S}^2g_{IS}^{-2}\tan^2\varphi)]. \quad (21)$$

Comparison of Eqs. (13) and (21) shows that this radiation field is equivalent to that produced by the γ_{eff} term in the effective surface polarization, provided that

$$\gamma_{eff}=-2\gamma. \quad (22)$$

PHYSICAL MODELS FOR EFFECTIVE NONLINEAR SURFACE POLARIZATION

The second-harmonic generation of light at the boundary of media with inversion symmetry has been observed from a variety of materials.[1] Bloembergen and coworkers[2,9] discussed the generated harmonics in terms of a bulk magnetic dipolar term and surface-type quadrupolar terms arising from the rapid variation of the normal component of the electric field over the transition region at the boundary of the medium. It is tacitly assumed in their analysis that these surface terms can also be described by the terms in Eq. (19) with three constants. Detailed calculation[10] shows that for a system of symmetrically bound electrons, $\alpha=-2\gamma$ and $\beta=0$. Actually, the electrons within the transition region near the surface are far from being symmetrically bound. One expects that the effects associated with the self-consistent surface potential and surface states may spoil the equality between the coefficients α and -2γ, and may allow β to assume a nonzero value.

The effective nonlinear surface polarization may also be regarded as an electric-field-induced second-harmonic polarization associated with the presence of a strong electric double layer at the surface. In alkali halides, the presence of this double layer is brought about largely through the displacement of the ions at the surface,[11] whereas in metals the double layer exists because of the ability of the electrons to extend themselves beyond the boundary of the host lattice.[12] In general, the presence of an adsorbed layer at the surface also influences the strength of the double layer.

In the presence of an electric double layer at the surface, the effective nonlinear surface polarization may be given by[13]

$$P_i^{S2}(2\omega)=a\langle E_i(\omega)n_jE_j(\omega)\rangle+bn_i\langle E_j(\omega)E_j(\omega)\rangle, \quad (23)$$

where the constants a and b are determined by the coefficients for electric-field-induced second-harmonic generation[14] and the strength of the electric double layer at the surface. Rough calculation indicates that these coefficients are of the right order of magnitude to explain the observed effects. Equation (23) is written such that the quantity inside the bracket $\langle\ \rangle$ is averaged over the extent of the double layer. However, these average values are very sensitive to the detailed variation of the dielectric constant within the layer, and the local-field corrections for both the linear and nonlinear coefficients may be quite different within the surface double layer than in the bulk. Extreme care must thus be taken to relate these surface coefficients to the bulk coefficients. Define

$$[(a+b)\langle E_z^2(\omega)\rangle-bE_z^2(\omega)]/E_z^2(\omega)=\tfrac{1}{2}(\epsilon_S^2-1)\alpha_S, \quad (24)$$

$$a\langle E_z(\omega)\rangle/E_z(\omega)=(\epsilon_S-1)\beta_S, \quad (25)$$

$$2\epsilon_T(\epsilon_S-1)b=\gamma_S; \quad (26)$$

one then obtains the corresponding surface polarization as follows:

$$P_z^{S2}(2\omega)=\tfrac{1}{2}(\epsilon_S^2-1)\alpha_SE_z^2(\omega)-(\gamma_S/2\epsilon_T)E^2(\omega), \quad (27)$$

$$P_{x,y}^{S2}(2\omega)=(\epsilon_S-1)\beta_SE_z(\omega)E_{x,y}(\omega). \quad (28)$$

EXPERIMENTAL

The experiments were performed with the unfocused light beam near 6940 Å from a ruby laser Q switched by a rotating prism and fired at a repetition rate of one pulse per second. The output from the laser was approximately 30 mJ in energy, 0.05 cm² in cross section, and 100 nsec in duration. The experimental arrangement

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[9] N. Bloembergen and R. K. Chang, in *Physics of Quantum Electronics*, edited by P. L. Kelley, B. Lax, and P. E. Tannenwald (McGraw-Hill Book Co., New York, 1966), p. 80; N. Bloembergen, R. K. Chang, and C. H. Lee, Phys. Rev. Letters 16, 986 (1966).
[10] C. C. Wang and G. W. Ford (to be published). Our results are different from those in Ref. 8 obtained with a somewhat different model.
[11] K. Lehovec, J. Chem. Phys. 21, 1123 (1953).
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TABLE I. Values of the nonlinear coefficients α_{eff}, β_{eff}, and γ_{eff} describing the effective nonlinear surface polarization of several liquids.

Liquid	α_{eff}/β_{eff}[a]	β_{eff} (10^{-16} esu)	γ_{eff} (10^{-16} esu)
Water	1.5±0.4	0.21	0.06
Acetone	1.6±0.6	0.17	0.06
Benzene	1.4±0.3	0.22	0.09
CS_2	1.3±0.3	0.31	0.16
Bromonaphthalene	1.2±0.3	0.28	0.18

[a] See text.

is depicted schematically in Fig. 2. The output from the laser is incident upon the liquid-air interface with its state of polarization determined by the orientation of the half-wave plate and Glan-laser prism; the second-harmonic wave reflected from the interface is analyzed with a polarizing prism, filtered through a cell of $CuSO_4$ solution and spectrometer, and detected with a high-gain photomultiplier combined with ADC and scaler circuits. The liquids used are of spectroscopic quality, and are distilled and filtered into an enclosed stainless-steel cell with a teflon lining.

The signal level for most liquids amounts to about 10 photoelectrons per 1000 laser shots. The background count for the present investigation has been reduced to less than one photoelectron per 1000 laser shots. The values of the harmonic power measured represent an average over as many as up to 6000 laser shots so that the uncertainty for each measurement is reduced to about 30%.

The power and the state of polarization of the second-harmonic waves were measured with the laser beam incident at an angle $\theta_i = 51°$ and with the electric vector polarized either at 45° or at 90° to the plane of incidence. For benzene, CS_2, and bromonaphthalene, the results were reproducible to within the statistical uncertainty; efforts to obtain reproducible results from water and acetone were unsuccessful, as results seemed to vary over a wide range from sample to sample, and from day to day for a given sample. For this reason, only results obtained with freshly prepared samples are quoted for these liquids.

Using Eqs. (13) and (14) and the refractive-index data available in the literature,[15] the coefficients α_{eff}, β_{eff}, and γ_{eff} deduced from the measured values of the harmonic waves are tabulated in Table I. The uncertainty in the values of α_{eff}/β_{eff} are *not* due to experimental errors, but results from our failure to determine the relative phase of γ_{eff} and β_{eff}. The negative sign should be taken if γ_{eff} and β_{eff} are of the same sign.

DISCUSSIONS

One observes from Table I that the effective nonlinear coefficients for liquids are generally smaller than those for solids[1,16] with comparable linear refractive indices (Table II). As these coefficients are really characteristic of a given surface, one expects that these differences in the coefficients are at least partly due to the differences in the detailed structure of the surfaces such as the differences in the surface double layer and in the adsorbed layer of foreign atoms or molecules at the surface.

It is felt that the difficulty with which to obtain reproducible results from water and acetone surfaces probably stems from contamination of the surfaces. Bloembergen *et al.*[2] have pointed out that surface harmonics should be particularly sensitive to variations in the conditions of the surface for low index materials; however, such sensitive dependence was not observed in low index solids and nonpolar liquids such as benzene. Ideally, it would be desirable to study the harmonics generated from surfaces under a variety of controlled conditions, thus permitting separate determination of various contributions to the harmonics. At present, experimental capabilities do not seem to allow such a determination. The fact that reproducible results are obtainable for many solids and liquids seems to indicate, however, that in most cases the adsorbed layer contributes very little to the observed surface harmonics.

One also observes from Tables I and II that the coefficient γ_{eff} is always small for liquids as well as for transparent insulating solids. This result may be either due to the incomplete cancellation of the harmonic waves generated, respectively, by the longitudinal bulk term in Eq. (22) and by the term in Eq. (26) arising from the electric double layer at the surface, or due to the smallness of both of these two terms. Although it is not possible to predict accurately the ratio of α_{eff}/β_{eff} for the case when the electric double layer alone contributes to the surface harmonics, rough calculation

TABLE II. Values of the nonlinear coefficients α_{eff}, β_{eff}, and γ_{eff} describing the effective nonlinear surface polarization of several solids.

Material	α_{eff}/β_{eff}	β_{eff} (10^{-16} esu)	γ_{eff} (10^{-16} esu)
CaF_2	4.0	0.4	a
BaF_2	3.1	0.4	a
NaF	5.1	0.5	a
LiF	4.0	0.5	a
Fused silica	3.5	0.5	a
BSC glass	2.9	0.5	a
KBr	2.5	0.45	a
KCl	2.9	0.6	a
NaCl	2.3	0.55	a
KI	1.8	1.0	0.4
MgO	1.4	1.2	0.5

[a] Estimated to be less than 0.2×10^{-16}.

[15] *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Co., New York, 1963), Sec. 6.

[16] As noted earlier, a multiplying factor of $\frac{1}{2}\epsilon_T(\epsilon_S+1)$ should be reinstated for the α term in Eq. (4) of Ref. 1. Thus, in Table II of Ref. 1, the column for β should be interpreted as that for β_{eff}; the column for γ should be interpreted as that for γ_{eff}; and the column for α/β should be divided by $\frac{1}{2}\epsilon_T(\epsilon_S+1)$ to obtain the corresponding values for α_{eff}/β_{eff}. The corrected values of these coefficients are included here as Table II.

based on a smooth variation of the dielectric constant over the transition region gives results in agreement with the measured values of this ratio to within a factor of 2. Whereas the model of electric double layer at the surface needs to be developed further to afford a close comparison with the experiments, the observations in this paper show that, for transparent insulators, the electric-field-induced second-harmonic generation within the surface double layer is probably more important than the quadrupolar nonlinearities. This effect due to the surface double layer may also be important in the reflected harmonics from the boundary of metals and semiconductors.[2,9]

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Measurement of $(\partial P/\partial T)_V$ and Related Properties in Solidified Gases. II. Solid H_2†

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We report measurements and their analysis of pressure changes with temperature and ortho-H_2 concentration in solid H_2 in both the hcp and cubic phases. The temperature range extended from 0.4 to 4.2°K, and the concentration c of ortho-H_2 was between 0.005 and 0.94. The measurements were carried out by means of a sensitive capacitance strain gauge capable of resolving pressure changes of 2×10^{-5} bar. The categories of experiments performed were (1) determination of the pressure P in the hcp phase as a function of ortho concentration at several temperatures; (2) determination of the pressure difference P (hcp) $-P$-(cubic) as a function of ortho concentration, and study of the hysteresis in both pressure and temperature of the hcp-to-cubic transition; and (3) measurement of $(\partial P/\partial T)_V$ at constant ortho concentration in the hcp phase at several different ortho concentrations. The results were analyzed in terms of a lattice contribution and an electric quadrupole-quadrupole (EQQ) interaction, neglecting any effects from other interactions and from crystalline fields. The EQQ interaction parameter determined experimentally was $\Gamma=6e^2Q^2/25R^5$, where eQ is the quadrupole moment of the orthomolecule in the state $J=1$, and R is the nearest-neighbor distance. The theoretical value for a rigid lattice is $\Gamma/k_B=1.00$°K. The results from (1) and (2), extrapolated to pure ortho-H_2, were analyzed using the theory of Miyagi and Nakamura and gave $\Gamma/k_B=0.82\pm0.04$°K (value extrapolated to $P=0$). This value was confirmed from the temperature of the maximum of $(\partial P/\partial T)_V$ at low ortho concentrations. The discrepancy between the experimental and the theoretical values of Γ is briefly discussed. From $(\partial P/\partial T)_V$ data with almost pure para-H_2 and from comparison with specific-heat data due to Ahlers, a lattice Grüneisen constant $\gamma_L=2.06\pm0.1$ was found. The Grüneisen constant of the EQQ interaction was found to be $\gamma_{EQQ}=1.62\pm0.1$, in agreement with the theoretically expected value. Evidence was found for redistribution of orthomolecules at low ortho concentration as a function of time. The theoretical expectations for a thermodynamic-equilibrium distribution of molecules in the lattice and that for a random high-temperature distribution are compared with experimental results.

I. INTRODUCTION

IN the last few years, there has been a great deal of theoretical interest in the molecular ordering occurring in the cubic and hcp phases for pure ortho-H_2 and ortho-para mixtures.[1–7] These studies were prompted in part by recent experimental work showing a first-order crystalline phase transition in both solid H_2 [8,9] and solid D_2 [9,10] at high ortho-H_2 and high para-D_2 concentrations, respectively. It is now generally believed that the electric quadrupole-quadrupole (EQQ) inter-

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