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Infrared spectral properties of hydrogen, deuterium, and tritium in TiO_2†

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Infrared spectra of TiO_2 single crystals containing either hydrogen, deuterium, or tritium were measured at 300, 77, and 8 K. Bands observed at 3276, 2437, and 2065 cm^{-1} near 300 K are, respectively, assigned to OH^-, OD^-, and OT^- based on a two-term anharmonic-oscillator model of the hydrogenic species. The frequencies were also analyzed by using a linear hydrogen-bonded model with harmonic forces, but the correlation between frequencies and bandwidths was at variance with that of known H-bonded systems. The absorption strength per ion of OT^- was calculated at several levels of approximation, and the best value determined was $a_T = 9.24 \times 10^{-18}$ cm. The harmonic and anharmonic mean-square displacements of OH^-, OD^-, and OT^- were calculated, and the differences between these quantities reflect the changes in the infrared bandwidths with reduced mass.

I. INTRODUCTION

The defect associated with hydrogen is known to be related to the electrical and mass transport properties of rutile. Several spectroscopic investigations of H and D in TiO_2 have probed the structure of this defect, and references to the early literature are given in the papers by Johnson and co-workers.[1-3] In infrared measurements of TiO_2 doped with hydrogen, deuterium, and various impurity ions, Johnson *et al.*[1] observed a number of bands ascribed to absorption by hydrogenic species. In particular, the bands reported at 3279 and 2439 cm^{-1} from spectra recorded at 300 K were assigned to unassociated OH^- and OD^- species, respectively. These bands were observed to shift to higher frequencies and to narrow considerably as the temperature was lowered to 10 K. A quantity defined as the absorption strength per ion was determined for unassociated OH^- and OD^- in TiO_2 by Johnson, DeFord, and Shaner.[3] These quantities denoted by a_H and a_D allow the concentration of OH^- or OD^- in TiO_2 to be determined from the integrated intensities of the respective bands. However, in spite of the many studies of hydrogen and deuterium in TiO_2, key questions regarding the precise structure of the defect associated with these impurities and its interaction with the host lattice remain unanswered.

The purpose of this paper is to discuss the results of our measurements of the infrared bands of OH^-, OD^-, and OT^- in TiO_2. To the best of our knowledge, this will include the first report of the vibrational frequency of a tritiated species in a solid. The measured frequencies are analyzed on the basis of an anharmonic oscillator and a linear hydrogen-bonded model represented by $O-H \cdots O$ in which the forces are harmonic. From the anharmonic-oscillator model, it is shown that the agreement between the observed and calculated frequency of OT^- uniquely specifies the value of the reduced mass for the unassociated hydrogenated species. The previously reported values of a_H and a_D are used to calculate the dipole derivatives for the OH^- and OD^- vibrations, and these, in turn, are used to calculate a_T for OT^- based on the dipole moment function derived for a free OH^- ion by Cade.[4] The harmonic and anharmonic mean-square displacements are also calculated for OH^-, OD^-, and OT^-. These are found to be related to the observed mass- and temperature-dependent changes in the infrared bandwidths.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The specimens of TiO_2 were disks about 1.5-mm thick cut from large single-crystal boules (National Lead Co.). The disk faces were parallel to the (100) plane and were polished through 4/0 emery paper and lapped with 6-μ diamond paste. A light-blue coloration indicated that the crystal was slightly reduced. Infrared measurements showed that the as-received material contained about $2 \times 10^{17}/cm^3$ of OH^- (see below). The presence of water vapor during crystal growth by flame fusion may have been responsible for the formation of OH^-. Since the OH^- content was sufficiently high for the intended study, the as-received material was used without further treatment with H_2.

A sample of rutile containing deuterium (TiO_2:D) was prepared by heating a disk at 873 K for 5 h under a pressure of about 0.4 atm of D_2. In order to restore the transparency of the sample, it was then heated for 2 h at 1073 K in a flowing stream of oxygen. The tritium-doped sample (TiO_2:T) was prepared by sealing a disk along with a compact of Cu_2O-CuO in an evacuated quartz ampoule. The ampoule was heated for 8 h at 1073 K. At this temperature, the oxygen pressure in the ampoule was about 2×10^{-3} atm. This pretreatment of the sample assured its stoichiometry. Following this process, the sample was reencapsulated along with the Cu_2O-CuO compact in a quartz ampoule, which was then evacuated and backfilled with about 0.2 Ci of tritium. The ampoule was then heated for 2 h at 1073 K. The high O_2 pressure in the ampoule during heating resulted in a sufficiently transparent sample for the infrared measurements. Following these measurements, the TiO_2:T sample was sectioned, the sections were dissolved in sulfuric acid, and the total tritium in each section was determined by liquid scintillation counting techniques. The total amount of tritium as determined by this procedure was 1.01×10^{16} (± 15%), which, on dividing by the sample volume, gives $n_T = 4.29 \times 10^{16}/\text{cm}^3$.

The infrared spectra were recorded with a Fourier-transform (interferrometric) spectrometer (Digilab Model No. FTS-20). The theoretical resolution was 1.0 cm^{-1} for the measurements at 300 K and 0.5 cm^{-1} for the measurements at 77 and 8 K. In a typical run, 800 scans of the sample were collected, and the resulting single-beam spectrum was ratioed with a reference spectrum of the empty, evacuated optical chamber. For the low-temperature measurements, the samples were mounted on the cold stage of an optical cryostat fitted with KBr windows. The cryostat was supported on the optical chamber of the spectrometer by a thick sheet of Plexiglas. O-ring seals to the vacuum shroud and the top of the chamber were provided so that the chamber including the sample space could be evacuated. The single-beam spectrum of the empty evacuated cryostat was used as the reference spectrum for the low-temperature measurements.

The results obtained from the infrared measurements of the TiO_2:H, TiO_2:D, and TiO_2:T samples are illustrated in Figs. 1 and 2. In Fig. 1, the ratioed spectrum of each sample was plotted as percent transmission and expanded to fill the ordinate scale. In Fig. 2, the ratioed spectra of TiO_2:T at 300 and 77 K were plotted as percent transmission according to the same scale. The measured peak frequencies, bandwidths (full width at one-half band maximum), and integrated intensities of the OH^-, OD^-, and OT^- bands at the three temperatures are given in Table I. Based on measurements of several rotational fine structure lines of CO_2 and H_2O, the frequencies of the sharp bands reported at 77 and 8 K in Table I are accurate to ±0.5 cm^{-1}. The integrated intensities represent $\int \log_{10}[I_0/I(\nu)]\, d\nu$ in cm^{-1}, where I_0 is the base-line transmission, and $I(\nu)$ is the transmission at frequency ν (cm^{-1}). These were determined by weighing cutout recordings of the band area, and from repeated determinations, the areas were accurate to about ±3%. From the study of TiO_2:H crystals by Soffer,[5] it was found that the OH^- band (reported at 3277 cm^{-1} at 300 K) was highly dichroic, such that the absorption coefficient for $\vec{E} \perp c$ was more than seven times larger than that for $\vec{E} \parallel c$. The radiation incident on the sample

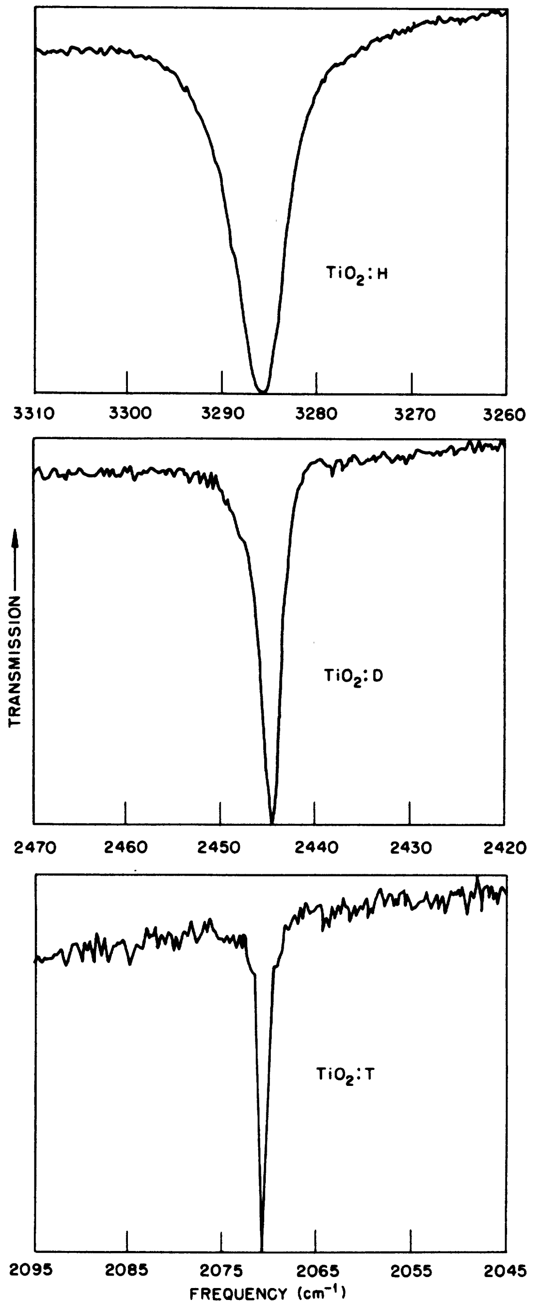

FIG. 1. Infrared bands of OH^-, OD^-, and OT^- in TiO_2 recorded at 77 K.

in the Fourier-transform spectrometer is elliptically polarized as a result of several reflections from mirrors. Therefore, for measurements of the band intensities, the samples were oriented so that the crystallographic *a* axis was parallel to the direction of maximum intensity of the incident radiation, i.e., the vertical axis.

III. DISCUSSION

A. Isotopic frequency shifts

A calculation of the frequency shift with the substitution of the hydrogen isotope in TiO_2 requires that two assumptions be made: (i) the atoms (other than hydrogen) involved in the local mode must be specified in order that the reduced mass can be calculated, and (ii) a model for the potential energy function of the local mode must be selected. If, for example, as reported by Soffer[5] the hydrogen species is assumed to be a diatomic OH^- ion and if the potential is taken to be harmonic, then the calculated ratios, ν_H/ν_D and ν_H/ν_T, are given by $(\mu_{OD}/\mu_{OH})^{1/2} = 1.374$ and $(\mu_{OT}/\mu_{OH})^{1/2} = 1.638$, respectively, where μ is the reduced mass.[6] From Table I, the observed ratios at 300 K are $\nu_H/\nu_D = 1.344$ and $\nu_H/\nu_T = 1.586$. Prior to our work, only the ν_H/ν_D ratio was known, and it was remarked by Johnson *et al.*[1] that the discrepancy between the observed and calculated ν_H/ν_D ratio indicated a relatively large anharmonicity in the OH^- potential. Without knowledge of the tritium frequency, however, it was not possible to test a potential energy model of the H-containing species.

Before discussing an analysis of the isotopic frequency shifts in terms of an anharmonic diatomic oscillator, it might be considered that the differences between the observed and calculated frequency ratios result from an incorrect choice of the reduced mass rather than an incorrect potential. This proposition was tested by assuming a harmonic diatomic oscillator, X-H. The mass of X determined from the observed ratio ν_H/ν_D, was $M_X = 8.346$ amu, and the calculated ratio of the X-H and X-T frequencies was $(\mu_{XT}/\mu_{XH})^{1/2} = 1.572$. Although this calculated frequency ratio is in better agreement with the observed value than that obtained by assuming a harmonic OH^- model, a nonsensical result is obtained for M_X. Moreover, the calculated frequency, $\nu_T = 2084$ cm^{-1}, differs by almost 20 cm^{-1} from the observed value.

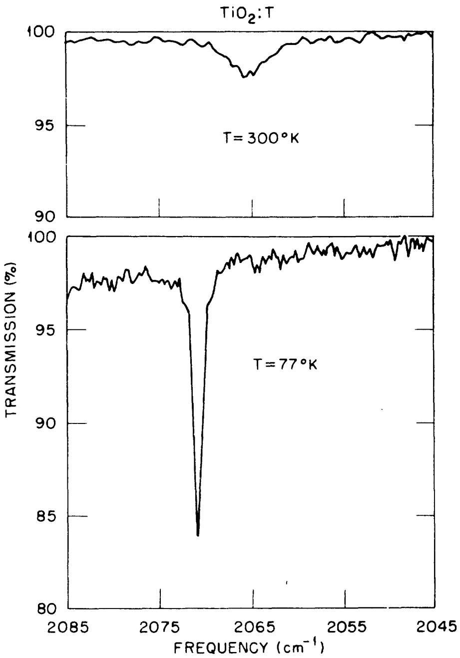

FIG. 2. Comparison of the infrared band of OT^- recorded at 300 and at 77 K.

A general method for calculating the isotopic frequency shift of a diatomic anharmonic oscillator has been described by Herzberg.[7] If the energy levels of one isotope are represented by the term value formula,

$$G_e(v) = (v+\tfrac{1}{2})w_e - (v+\tfrac{1}{2})^2 w_e x_e + (v+\tfrac{1}{2})^3 w_e y_e + \cdots , \quad (1)$$

then the energy levels of the other isotope are

TABLE I. Frequencies (ν), bandwidths (δ),[a] and integrated intensities ($\bar{A}$)[b] of the OH^-, OD^-, OT^- bands in TiO_2:H, TiO_2:D, and TiO_2:T, respectively.

	TiO_2:H			TiO_2:D			TiO_2:T		
T (°K)	300	77	8	300	77	8	300	77	8
ν (cm^{-1})	3276	3286	3286.5	2437	2445	2445	2065	2071	2070.5
δ (cm^{-1})	20.0	7.0	7.0	8.0	1.90	2.0	4.5	1.00	1.2
$\bar{A}$ (cm^{-1})	1.42	1.51	1.51	2.65	1.89	1.67	0.04	0.11	0.09

[a] Full width at one-half band maximum.

[b] Values of $\int \log_{10}(I_0/I(\nu))d\nu$, where I_0 is the base-line transmission and $I(\nu)$ is the transmission at frequency ν.

closely approximated by

$$G_e^i(v) = (v+\tfrac{1}{2})\rho_i w_e - (v+\tfrac{1}{2})^2\rho_i^2 w_e x_e + (v+\tfrac{1}{2})^3\rho_i^3 w_e y_e + \cdots , \qquad (2)$$

where v is the vibrational quantum number, w_e, x_e, and y_e are constants, $\rho_i = (\mu/\mu_i)^{1/2}$, and μ and μ_i are the reduced masses of respective isotopes. For $v=1$ and neglecting terms higher than quadratic, it can be shown that the vibrational frequencies obtained from Eqs. (1) and (2) are given by

$$\nu = w_e - 2w_e x_e \qquad (3)$$

and

$$\nu_i = \rho_i w_e - 2\rho_i^2 w_e x_e . \qquad (4)$$

The observed hydrogen and deuterium frequencies were used in Eqs. (3) and (4) to determine w_e and $w_e x_e$, where in Eq. (4), $\rho_i = (\mu_{OH}/\mu_{OD})^{1/2} = 0.7276$. These coefficients belong to the hydrogen isotope, and those for OD^- and OT^- are given by $w_e^i = \rho_i w_e$ and $w_e^i x_e^i = \rho_i^2 w_e x_e$, where ρ_i^2 is the appropriate ratio of the reduced masses. For OT^-, $\rho_i = 0.6104$.

The values of w_e^i and $w_e^i x_e^i$ coefficients obtained from a fit of Eqs. (3) and (4) to the 300- and 77-K TiO_2:H and TiO_2:D data are given in Table II. Because the 8-K results are nearly equal to those obtained at 77 K (Table I), these were excluded from analysis. The calculated OT^- frequencies are given by $\nu_T = w_e^T - 2w_e^T x_e^T = 2063.7$ cm^{-1} at 300 K and $\nu_T = 2070.3$ cm^{-1} at 77 K. From Table I, these calculated values agree very well with the observed frequencies, the difference amounting to 1.3 cm^{-1} at 300 K (0.06% error) and 0.7 cm^{-1} at 77 K (0.02% error). The harmonic and anharmonic coefficients of OH^- in TiO_2 are seen to be quite different from those of OH^- in KBr, which were reported to be[8] $w_e = 3789$ cm^{-1} and $w_e x_e = 85.5$ cm^{-1} at 78 K. Thus, based on this model, the OH^- potential in rutile is much more anharmonic than was found in the alkali halides and, together with the fact that w_e is much smaller than OH^- in rutile, suggests a larger nonbonded interaction between the proton and neighboring ions.

The availability of the tritium data provides a means of determining, within certain limits, whether or not the reduced mass of the H-containing species can be uniquely specified. The question is, using the anharmonic oscillator model described above, will any other choice of the reduced mass (i.e., other than μ_{OH}, μ_{OD}, and μ_{OT}) result in a calculated ν_T frequency in equally good agreement with the observed value? This question can be addressed if it is assumed that, for any choice of a structural model for the hydrogen defect in TiO_2, the mode involving displacement of the proton does not interact with any other local mode of this defect. This approximation is reasonable in view of the high frequency of this vibration.[9] The hydrogen displacement mode can then be characterized by an effective reduced mass, $\mu_{XH} = M_X M_H/(M_X + M_H)$, and the problem can thus be treated as a diatomic oscillator. In order to determine the effect of a change in reduced mass on the calculated tritium frequency, Eqs. (3) and (4) were used with $\rho = (\mu_{XH}/\mu_{XD})^{1/2}$. It was convenient to express M_X in terms of the mass of oxygen, i.e., $M_X = nM_O$ where n is a number. For each value of n, w_e and $w_e x_e$ were calculated from Eqs. (3) and (4), and these in turn were used in Eq. (4) with $\rho_i = (\mu_{XH}/\mu_{XT})^{1/2}$ to calculate ν_T.

The results of the calculations are presented graphically in Fig. 3, where values of ν_T are plotted versus n. The upper horizontal line in this figure indicates the observed frequency, and the lower horizontal line indicates the frequency calculated for an infinite effective mass of X. The latter situation represents a tritium atom vibrating against a fixed mass. As seen in Fig. 3, the curve of calculated frequencies intersects the observed frequency line at $n=1$, which corresponds to a diatomic OT^- species. This shows that, within the approximation made in these calculations, the reduced mass of the vibrating species can be uniquely specified.

Other spectroscopic constants of OH^-, OD^-, and OT^- derived from the w_e and $w_e x_e$ coefficients are also listed in Table II. The term value expression $G_0(v) = w_0 v - w_0 x_0 v^2$ is convenient for calculat-

TABLE II. Spectroscopic constants for OH^-, OD^-, and OT^- in TiO_2 at 300 and 77 K.[a]

	T (°K)	w_e (cm^{-1})	$w_e x_e$ (cm$^-$)	D_e (eV)	w_0 (cm^{-1})	D_0 (eV)
OH^-	300	3545.14	134.57	2.89	3410.57	2.68
	77	3557.48	135.74	2.89	3421.74	2.67
OD^-	300	2579.44	71.24	2.89	2508.20	2.74
	77	2588.42	71.86	2.89	2516.56	2.73
OT^-	300	2163.95	50.14	2.89	2113.81	2.76
	77	2171.48	50.58	2.89	2120.90	2.76

[a] Constants derived from the OH^- and OD^- data.

ing the energy levels of these species where $w_0 = w_e - w_e x_e$ and $w_0 x_0 = w_e x_e$. The quantities $D_e = w_e^2/4w_e x_e$ represent the energy from the bottom of the potential well to the edge of the dissociation limit, and $D_0 = w_0^2/4w_0x_0$ is the dissociation energy of the molecules.[7,10] The D_0 values are equal to or greater than the heats of dissociation.[10] From the data reported by Wedding and Klein[8] for OH^- in KBr, we find that $D_0 = 4.97$ eV. Thus, based on the above model, the binding energy of OH^- in KBr is nearly twice as large as it is in TiO_2.

From one of the earlier studies of hydrogen and deuterium in TiO_2, Johnson *et al.*[1] reported a weak band at 4350 cm^{-1} in the spectrum of TiO_2:H at 300 K and tentatively assigned it to the first overtone of the fundamental reported at 3279 cm^{-1}. It was noted that this assignment implies a large anharmonicity since the harmonic frequency of the overtone should occur at 2×3279 $cm^{-1} = 6558$ cm^{-1}. The calculated value of the first overtone of OH^- at 300 K based on the diatomic anharmonic-oscillator model is $G_0^H(2) = 6283$ cm^{-1}. Thus the 4350-cm^{-1} band cannot be due to $2\nu_H$ according to this model.

It has been remarked by Soffer[5] that the stretching frequency of OH^- in TiO_2:H (3276 cm^{-1}) as compared to those of OH^- groups in other systems was evidence for hydrogen bonding[11] in rutile. In order to determine whether or not an alternate model based on hydrogen bonding could account for the isotropic frequency shifts, we calculated the OT^- frequency based on a linear harmonic model, O–H $\cdots X$, using two force constants, k_1 for Δr_{OH} and k_2 for Δr_{HX}, and assuming that X remains fixed. With the latter constraint, it can be shown that the eigenvalues are given by the roots of

$$\lambda^2 - \left(\frac{k_1}{\mu_i} + \frac{k_2}{m_i}\right)\lambda + \frac{k_1 k_2}{m_O m_i} = 0 , \tag{5}$$

where $\mu_i = m_i m_O/(m_i + m_O)$ and $m_i = m_H$, m_D, or m_T. Of the two roots of this equation,

$$\lambda_\pm = \frac{1}{2}\left(\frac{k_1}{\mu_i} + \frac{k_2}{m_i}\right) \pm \frac{1}{2}\left[\left(\frac{k_1}{\mu_i} + \frac{k_2}{m_i}\right)^2 - \frac{4k_1k_2}{m_O m_i}\right]^{1/2} , \tag{6}$$

$\lambda_\pm$ corresponds to the hydrogen stretching mode denoted by λ_i, and λ_- corresponds to the vibration of the OH^- group against X in which r_{OH} remains fixed. We assumed that the force constant k_1 was fixed by the frequency ν_0 of a "free" OH^- species (i.e., $k_2 = 0$). For any choice of ν_0, $\lambda_0 = (2\pi c \nu_0)^2$ and $k_1 = \mu_H \lambda_0$. With the value of k_1 fixed by λ_0, Eq. (6) was solved for the value of k_2 which yielded the observed eigenvalue of the OH^- stretching frequency, λ_H:

$$k_2 = \lambda_H\left(\frac{k_1}{\mu_H} - \lambda_H\right)\left(\frac{m_O m_H}{k_1 - \lambda_H m_O}\right) , \tag{7}$$

where $\lambda_H = 3.813 \times 10^{29}$ sec^{-2}. The value of k_2 from Eq. (7) and the previously set value for k_1 were used to calculate the OD^- stretching eigenvalue from Eq. (6). This process was repeated in order to generate a set of such calculated eigenvalues, and these were plotted versus ν_0 to determine the set of parameters which gave the best fit to $\lambda_D = 2.110 \times 10^{29}$ sec^{-2} ($\nu_D = 2437$ cm^{-1}). With $\nu_0 = 3825$ cm^{-1}, $k_1 = 5.198 \times 10^5$ dynes/cm and $k_2 = -2.500 \times 10^5$ dynes/cm, the calculated OD^- stretching frequency was $\nu_D = 2436$ cm^{-1}, and the calculated OT^- stretching frequency was $\nu_T = 2079$ cm^{-1}. A comparison with the 300-K data in Table I shows that the latter quantity is 15 cm^{-1} higher than the observed value.

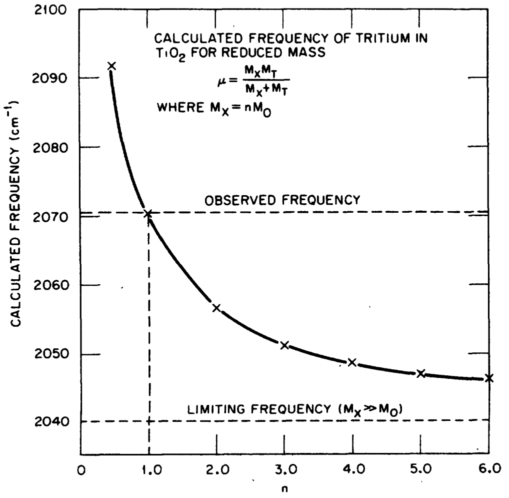

FIG. 3. Graph of the OT^- stretching frequency vs the factor $n = M_X/M_O$ where M_O is the mass of oxygen. Frequencies were calculated from the diatomic anharmonic-oscillator model.

The results from the above analysis suggest that a more realistic H-bounded model based on potentials of the type formulated by Lippincott and Schroeder[12] for the O–H and OH $\cdots$O interactions might yield a calculated tritium frequency in equally good agreement with the observed value as obtained from the diatomic anharmonic-oscillator model. However, there are serious discrepancies between the observed frequencies and widths of the infrared bands in rutile compared to those expected in H-bounded systems.[11,12] As noted by Johnson *et al.*[1] the large dichroism of the OH^- bands in rutile observed by Soffer[5] shows that OH^- lies in the (001) plane. From the crystal structure parameters of rutile,[13] the first- and second-nearest-neighbor O $\cdots$O distances in the (001) plane are calculated as 2.530 and 3.327 Å, respectively. Based on a graphical correlation between the shift in OH^- stretching frequency with O $\cdots$O distance in solids,[11] the 2.530-Å separation would result in a downward shift of about 1300 cm^{-1}, while the 3.327-Å separation would result in virtually no shift. If a nominal value of the free OH^- stretching frequency[11] is taken to be 3600 cm^{-1}, the observed shift in rutile, $\Delta\nu_s = 3600 - 3276 = 324$ cm^{-1}, requires an O···O separation of about 2.75 Å. Based on the correlation found between the frequency shift and the bandwidths,[11] $\Delta\nu_s \geq 300$ cm^{-1} requires a width of greater than 200 cm^{-1}. Furthermore, as the O···O distance presumably decreases as the temperature is lowered from 300 to 8 K, the hydrogen stretching frequency should decrease and the bandwidth should increase. These requirements of the linear-hydrogen-bond model are clearly inconsistent with the observed data in Table I suggesting that either (i) a linear O–H···O bond does not form in TiO_2:H or (ii) the H bond in rutile is unique.

Although a H-bonded model of OH^- in TiO_2 could be developed to give quantitative agreement with the observed frequencies, it is evident that the characteristics of the OH^-, OD^-, and OT^- bands in rutile are at variance with those of known hydrogen-bounded OH groups in other solids.[11] On the other hand, the anharmonic diatomic oscillator model was able to predict the ν_T frequency nearly within the experimental uncertainty of the measurement. Further tests of this model could be made by observing the overtone frequencies of OH^-, OD^-, and OT^-. Perhaps a more rigorous test of these models might be made from a quantum-mechanical calculation of frequencies and intensities of the infrared absorption bands, but this is beyond the scope of the present work.

B. Band intensities

A quantity termed the absorption strength per ion was determined for OH^- and OD^- in TiO_2 in the earlier work by Johnson *et al.*[3] This quantity is defined by $a_i = \overline{A}_i / t n_i$, where $\overline{A}_i = \int \log_{10}[(I_0/I(\nu)]\, d\nu$ is the integrated intensity defined above, t is the sample thickness in cm, and n_i is the number of ions per cm^3. The values reported were $a_H = 2.51 \times 10^{-17}$ cm for OH^- and $a_D = 1.33 \times 10^{-17}$ cm for OD^-. These values were used with the integrated intensities given in Table I and the disk thickness to calculate n_H and n_D reported in Table III. It will be noted in this table that the OH^- content differed among the TiO_2:H, TiO_2:D, and TiO_2:T samples. The OH^- content of the as-received TiO has been observed to vary from one boule to another and also along the axis of growth of a given boule. These variations could arise from changes in the flame composition during the growth process and should account for the different n_H values shown in Table III. The TiO_2:H and TiO_2:T samples were nonadjacent disks cut from the same boule, and the TiO_2:D sample was prepared from a second boule.

The concentration of tritium determined from the liquid scintillation counting procedure ($n_T = 4.29 \times 10^{16}/cm^3$) may not accurately represent the number density of OT^- in the sample because some of the tritium counted might be due to T_2 molecules trapped in the lattice. Therefore, it is of interest to have an independent determination of the OT^- concentration from the measured integrated intensity of the infrared band. For this determination, it is necessary to know a_T. We have calculated this quantity from the reported values[3] of a_H and a_D using several levels of approximation. The highest level of approximation is based on the results due to Cade.[4] In this work, the molecular properties of an isolated OH^- ion were calculated using Hartree-Fock wave functions. It was shown that the dipole moment P is a polynomial function of the internuclear displacement $r - r_e$, where r_e is the equilibrium internuclear distance, and could be well represented by a simple parabola centered about the maximum of P (see Fig. 5 of Ref. 11). It was also shown that, because of the formal charge, the dipole moment of OH^- was dependent on the choice of the origin of the coordinate system. For example, if $P_{\text{c.m.}}$ and P_{gc} denote the dipole moment for the origin at the center of mass and at the geometric center, respectively, then for OH^-,

$$P_{\text{c.m.}}(r) = P_{\text{gc}}(r) - \tfrac{1}{2} b r \left[\frac{m_O - m_H}{m_O + m_H} \right], \tag{8}$$

where b is a constant.[14] The important quantity

TABLE III. Calculated number densities and dipole derivatives of OH^-, OD^-, and OT^- in TiO_2.

(A) Number densities (ions/cm^3)[a]	TiO_2:H	TiO_2:D	TiO_2:T	
n_H	3.0×10^{17}	8.9×10^{16}	8.8×10^{17}	
n_D		1.0×10^{18}		
n_T			2.6×10^{16} (4.3×10^{16})[b]	
(B) Dipole derivatives[c]	OH^-	OD^-	OT^-	
$\lvert dP/dr \rvert$	1.40	1.39	1.37	$(\times 10^{-10})$
$\lvert dP/dQ \rvert$	112.0	80.6	66.9	

[a] Number densities of OH^- and OD^- determined from the a_H and a_D quantities, respectively, reported by Johnson, *et al.*[3] The number density of OT^- determined from the calculated value of a_T as described in text.

[b] Number in parentheses determined from liquid scintillation counting of the TiO_2:T sample.

[c] Values based on 300-K data and corrected for the Lorentz field effect. $\lvert dP/dr \rvert$ in units of $g^{1/2}\,cm^{3/2}\,sec^{-1}$; $\lvert dP/dQ \rvert$ in units of $cm^{3/2}\,sec^{-1}$.

for calculating a_T is $(dP/dr)_{r_e}$, the dipole derivative evaluated at $r = r_e$, and from Eq. (8), this is expressed as

$$\left(\frac{dP_{\mathrm{c.m.}}}{dr}\right)_{r_e} = b_1 - b_2\left[\frac{m_O - m_H}{m_O + m_H}\right] , \tag{9}$$

where b_1 and b_2 are constants.[14]

The absorption strength per ion is related to the dipole derivative through a series of defining equations. From Eq. (2) of Ref. 3,

$$a_H = \frac{1}{2.303 n_H} \int \alpha(\nu) d\nu$$

$$= \frac{1}{t n_H} \int \log_{10}[I_0/I(\nu)] d\nu , \tag{10}$$

where $\alpha(\nu) = (1/t)\ln[I_0/I(\nu)]$ is the absorption coefficient. The absolute intensities of infrared bands are often expressed in terms of the quantity[15] $A = (1/C) \int \alpha(\nu) d\nu$, where C is the concentration in mole/cm^3. From the above definition, $A = 2.303\bar{A}/Ct$.

The equation expressing A in terms of $(dP/dQ)^2_{Q_e}$ has been given by Overend[15] for absorption of isotropic radiation by molecules in the gas phase. This equation must be modified for the present experiments which represent absorption of polarized radiation by OH$^-$ ions in either fixed or random orientations in the (001) plane. The appropriate expression can be obtained by following the standard derivation for induced dipole absorption and retaining only the term for radiation polarized along one axis. Using this term in Overend's treatment gives

$$A_i = \frac{8\pi^3 N \nu_i}{hc} \left|\langle 1 | \hat{k} \cdot \vec{\mathrm{P}} | 0 \rangle\right|^2 , \tag{11}$$

where N is Avagadro's number, ν_i is the observed peak frequency, and $\hat{k}$ is a unit vector parallel to the crystallographic $\vec{a}$ axis. In the harmonic approximation,

$$\left|\langle 1 | \hat{k} \cdot \vec{\mathrm{P}} | 0 \rangle\right|^2 = K \left(\frac{h}{8\pi^2 c w_e}\right)\left(\frac{dP}{dQ}\right)^2_{Q_e} , \tag{12}$$

where K is a geometric factor arising from $\hat{k} \cdot \vec{\mathrm{P}}$. If the dipole moments are randomly oriented in the (001) plane, then $K = (1/\pi)\int_0^\pi \cos^2\theta \, d\theta = \frac{1}{2}$, where θ is the angle between $\hat{k}$ and $\vec{\mathrm{P}}$. If the dipole moments have fixed positions along equivalent directions, then $K = \cos^2\theta$, and because there are an equal number of dipoles at angles θ and $\frac{1}{2} - \theta$, it follows that $k = \frac{1}{2}$. Thus, for all cases, it is found that

$$A_i = \frac{1}{n}\left(\frac{n^2+2}{3}\right)^2 \left(\frac{\nu_i}{w_e^i}\right) \frac{N\pi}{2c^2} \left(\frac{dP}{dQ}\right)^2_{Q_e} . \tag{13}$$

The factor $(1/n)[\frac{1}{3}(n^2+2)]^2$ is the Lorentz effective field correction.[16,17] We approximated this factor for TiO$_2$ by taking $n = 0.67 n_o + 0.33 n_e$ where $n_o = 2.37$ and $n_e = 2.55$ are the ordinary and extraordinary ray refractive indices, respectively, measured at 4 μ.[18] These give $n = 2.43$, and $(1/n)\frac{1}{3}(n^2+2) = 2.86$. Since the concentration (mole/cm^3) is given by $C_i = n_i/N$, and since $A_i = 2.303 N a_i$, then

$$a_i = 1.24 \left(\frac{\nu_i}{w_e^i}\right) \frac{\pi}{2c^2} \left(\frac{dP}{dQ}\right)^2_{Q_e} . \tag{14}$$

The normal coordinate Q is defined in terms of the interatomic displacement coordinate, $\Delta r = (r - r_e)$, by $Q = \mu^{1/2}\Delta r$ where Δr refers to center-of-mass coordinates. Since $dQ/d\Delta r = dQ/dr = \mu^{1/2}$,

$$\frac{dP}{dr} = \mu^{1/2} \frac{dP}{dQ} . \tag{15}$$

The values of a_H and a_D reported by Johnson *et al.*[3] and ν_H, ν_D, w_e^H, and w_e^D in Tables I and II, were used in Eq. (14) to calculate $|(dP/dQ)_{Q_e}|$ for OH$^-$ and OD$^-$. With $\mu_{OH} = 1.563 \times 10^{-24}$ g and $\mu_{OD} = 2.952 \times 10^{-24}$ g, the dP/dr quantities were determined from Eq. (15), and the calculated values of dP/dQ are given in Table III. The values of dP/dr can be compared with the respective dipole derivatives for OH$^-$ and OD$^-$ in KBr. From the data of Wedding and Klein,[8] we calculate $|dP/dr| = 2.404 \times 10^{-10}$ g$^{1/2}$ cm$^{3/2}$ sec^{-1} for OH$^-$ and $|dP/dr| = 2.39 \times 10^{-10}$ g$^{1/2}$ cm$^{3/2}$ sec^{-1} for OD$^-$, where $n = 1.559$ was used in the Lorentz effective-field correction.

The dP/dr quantities for OH$^-$ and OD$^-$ were used with the appropriate mass ratios in Eq. (9) to determine the constants b_1 and b_2. These were found to be $b_1 = \mp 1.273 \times 10^{-10}$ g$^{1/2}$ cm$^{3/2}$ sec^{-1} and $b_2 = \pm 0.144 \times 10^{-10}$ g$^{1/2}$ cm$^{3/2}$ sec^{-1}, where the sign is determined by the sign chosen for dP/dr. With these constants, Eqs. (9) and (15) yielded the values for dP/dr and dP/dQ of OT$^-$ given in Table III. From the appropriate values of dP/dr or dP/dQ, a_T can be calculated from the ratio a_T/a_H or a_T/a_D using Eq. (14). These ratios give $a_T = 9.24 \times 10^{-18}$ cm and $a_T = 9.25 \times 10^{-18}$ cm, respectively, which are listed under the column heading (1) in Table IV.

TABLE IV. Calculated values of the absorption strength per ion, a_T, for OT$^-$ in TiO$_2$.

	a_T (cm)[a]		
	(1)	(2)	(3)
(A)	9.24	9.66	9.36 ($\times 10^{-18}$)
(B)	9.25	9.45	9.36
Average	9.24	9.56	9.36 ($\times 10^{-18}$)

[a] The column numbers refer to the method used to calculate a_T, and the row letters designate that a_T was calculated from (A) a_T/a_H or (B) a_T/a_D.

The data in Table III show that $|(dP/dr)|$ is nearly the same for OH$^-$, OD$^-$, and OT$^-$. A reasonable approximation to a_T can be made by assuming dP/dr to be constant. With this assumption, the ratio a_T/a_i gives

$$a_T = \left(\frac{\nu_T}{w_e^T}\right)\left(\frac{w_e^i}{\nu_i}\right)\frac{\mu_i}{\mu_T}a_i , \tag{16}$$

where $i = $ H or D. The values of a_T calculated from Eq. (16) are listed under column (2) in Table IV. A check on the mutual agreement between the experimental values,[3] a_H and a_D, can be obtained from Eq. (16). Thus for $a_H = 2.51\times10^{-17}$ cm, Eq. (16) gives $a_D = 1.36\times10^{-17}$ cm, which agrees very well with the experimental value, $a_D = 1.33\times10^{-17}$ cm. By substituting the appropriate values of ν_i and w_e^i (Tables I and II, respectively), the product of the frequency ratios in Eq. (16) amount to 1.032 and 1.010 for a_T/a_H and a_T/a_D, respectively. Thus, a further approximation to a_T can be made by neglecting these ratios, and this gives the very simple relationship

$$a_T = (\mu_i/\mu_T)a_i . \tag{17}$$

The values of a_T obtained from Eq. (17) are also listed in Table IV (column 3), and these are seen to agree reasonably well with the values calculated from Eq. (14). It is interesting to note that, using the experimental value for a_H, Eq. (17) gives $a_D = 1.328\times10^{-17}$ cm, which essentially agrees exactly with the experimental value.

The number density of OT$^-$ in the TiO$_2$:T sample is given by $n_T = ta_T/\bar{A}_T$. We consider the "best" value of a_T to be the average of the two values given under (1) in Table IV, i.e., $a_T = 9.24\times10^{-18}$ cm. With $\bar{A}_T$ from Table I and the sample thickness, $n_T = 2.6\times10^{-16}/\text{cm}^3$. As shown in Table III, this value is comparable to the number density of tritium determined from the liquid scintillation counting procedure. The source of the discrepancy between the two values is not certain at present. One can speculate that the total tritium counted includes unreacted T or T$_2$ in the TiO$_2$ lattice so that it is not surprising that n_T determined by this procedure is higher than n_T determined from the infrared data, since the latter is a measure the concentration of OT$^-$.

C. Mean-square displacements and bandwidths

The mean-square displacements of OH$^-$, OD$^-$, and OT$^-$ in TiO$_2$ have been calculated because these quantities provide a direct measure of the localized motion of the respective ions and their interaction with the surrounding lattice.[19,20] The theoretical basis for calculating mean-square displacements in the harmonic approximation has been described in detail for molecules[21] and solids.[20] For diatomic molecules, the *msd* is denoted by $\langle r^2\rangle$, which represents the thermal average over all states of the expectation values, $\langle v|r^2|v\rangle = 2u_0(v+\frac{1}{2})$, where v denotes the vibrational quantum number and $u_0 = h/8\pi^2\mu c w_e$. The result of the thermal average is[21]

$$\langle r^2\rangle = u_0^2\coth(hcw_e/2kT) . \tag{18}$$

The effect of anharmonicity on the mean-square displacements of diatomic molecules has been investigated by Reitan.[22] The expectation values of q and q^2, where $q = (4\pi^2\mu c w_e/h)^{1/2}(r - r_e)$, were calculated with wave functions obtained by perturbation theory for a potential energy function including cubic and quartic terms and with the wave functions derived from a solution of the wave equation using a Morse potential.[23] The expressions given for the mean-square displacement quantities include (using Reitan's notation)

$$u_e^2 = \langle (r-r_e)^2\rangle = 2u_0^2\langle q^2\rangle \tag{19a}$$

and

$$u_a^2 = \langle (r-\bar{r})^2\rangle = 2u_e^2(\langle q^2\rangle - \langle q\rangle^2) , \tag{19b}$$

where $\langle q\rangle$ and $\langle q^2\rangle$ are the thermal average over all states of $(q)_v = \langle v|q|v\rangle$ and $(q^2)_v = \langle v|q^2|v\rangle$, respectively, and $\bar{r} = \langle v|r|v\rangle$. (For the harmonic oscillator, $u_e^2 = u_a^2 = \langle r^2\rangle$.) Equations were derived[22] for the expectation values expressed as functions of the spectroscopic constant x_e. For the case of OH$^-$, OD$^-$, and OT$^-$, it can be shown that only the $v = 0$ terms are important, and in this case, the respective quantities defined by Eqs. (19) have the same form for either anharmonic potential energy function. These are given by

$$u_e^2 = 2u_0^2(\tfrac{1}{2} + \tfrac{15}{8}x_e) \tag{20a}$$

and

$$u_a^2 = 2u_0^2(\tfrac{1}{2} + \tfrac{3}{4}x_e) . \tag{20b}$$

The mean-square displacements for OH$^-$, OD$^-$, and OT$^-$ were calculated from Eqs. (18) and (20), and the results are given in Table V. The effect of anharmonicity results (at maximum) in a 14% difference between u_e^2 and $\langle r^2\rangle$ and a 6% difference between u_a^2 and $\langle r^2\rangle$ for OH$^-$. By comparison, using the data of Wedding and Klein,[8] the percentage difference between u_e^2 and $\langle r^2\rangle$ and u_a^2 and $\langle r^2\rangle$ for OH$^-$ in KBr is about 8% and 3%, respectively.

The trends noted in the bandwidths reported in Table I were briefly commented upon earlier. These trends are more obvious on comparison of

TABLE V. Harmonic and anharmonic mean-square displacement of OH^-, OD^-, and OT^- in TiO_2 and a comparison of observed and calculated bandwidth ratios.

(A) Mean-square displacements (Å^2)

	$T=300$ K				$T=77$ K			
	$\langle r^2\rangle$	u_e^2	u_a^2		$\langle r^2\rangle$	u_e^2	u_a^2	
OH^-	5.05	5.77	5.34	($\times 10^{-3}$)	5.03	5.75	5.32	($\times 10^{-3}$)
OD^-	3.67	4.05	3.83		3.66	4.04	3.81	
OT^-	3.08	3.35	3.19		3.07	3.34	3.18	

(B) Ratios of infrared bandwidths

	300 K	77 K		$\delta(300)/\delta(77)$[a]
δ_H/δ_D	2.5	3.3	OH^-	3.2
δ_H/δ_T	4.4	6.2	OD^-	4.2
δ_D/δ_T	1.8	1.9	OT^-	4.5

	H/D	H/T	D/T[b]
$(u_e^4)_i/(u_e^4)_j$	2.0	3.0	1.5

[a] $\delta(300)/\delta(77)$ is the ratio of the bandwidths observed at 300 and at 77 K.

[b] The subscripts i and j refer to the hydrogen isotopes.

the ratios of these widths as given in Table V.

The sources of band broadening of the OH^-, OD^-, and OT^- species in rutile are intramolecular bonding effects and lattice interactions. In the former category, the influence of H bonding is apparently negligible for the reasons discussed earlier. The latter contribution to band broadening arises from anharmonic interaction of the impurity ion with the host, and mechanisms based on this interaction have been reviewed by Klein.[19] Because of the high local mode frequencies involved, it seems that phonon scattering should be the dominant mechanism. In this case, the ratio of $\langle r^2\rangle^2$ should approximate the bandwidth ratios, but we found that the values of $(u_e^4)_i/(u_e^4)_j$ $(i,j = \mathrm{H, D, T})$ given in Table V agreed slightly better with observed δ_i/δ_j ratios. The qualitative agreement between these quantities might indicate that indeed phonon scattering is an important contribution to the infrared bandwidths. However, the ratios of the widths measured at two temperatures for the same ion (Table V) suggest that decay of the local-mode vibrational excitation into multiphonons of the host lattice (perhaps a decay into a phonon continuum) is predominantly responsible for the bandwidths. More detailed studies of the temperature dependence of these widths will be required before the mechanisms contributing to the infrared bandwidths can be understood.

IV. SUMMARY AND CONCLUSIONS

The frequencies observed for the tritiated species in TiO_2 provided the data necessary for testing various models of the defect associated with hydrogen in rutile. Assuming this defect to be represented by a diatomic anharmonic oscillator yielded excellent agreement between the observed and calculated frequencies for OT^-. In order to account for the large frequency shift from a nominal value of ~3600 cm^{-1} for a free OH^- ion, a more complex model which properly treats the anharmonicity of the OH^- band and the anharmonic interactions of OH^- with the surrounding lattice will be required. While a model based on linear hydrogen bonding could account for this frequency shift in a rather simple way, the relationships between $O\cdots O$ distance, frequency shifts from the free ion value, and the bandwidths, which have been well established from studies of hydrogen bonding in solids, were seen to be violated for hydrogen and its isotopes in TiO_2. In spite of the remaining uncertainty with regard to a complete picture of the hydrogen-associated defect in rutile, the a_T quantity determined in this work is independent of any model of this defect, and, as stated above, the parameters determined for the simple diatomic anharmonic-oscillator model permit accurate calculation of isotropic frequency shifts.

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[*] Solid State Division.

[‡] Metals and Ceramics Division.

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