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The Effect of the Electrostatic Polarization of the Solvent on Electronic Absorption Spectra in Solution

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Regarding the solvent as a continuous dielectric medium, it is shown that its effect on the Franck-Condon absorption of light by solute molecules must be expressed in terms of the electronic polarization part of its dielectric constant, $K=n^2$. Using methods based both on quantum theory and on classical dispersion theory, it is shown that the red shift of absorption in solution depends directly on f , the oscillator strength, and inversely either on a^3 (a is the radius of the spherical solute molecule) or the polarizability α . The expression $\Delta\nu(\text{cm}^{-1}) = \text{const.} (f/\nu a^3)[(n^2-1)/(2n^2+1)]$ with two possible values of the constant, and alternatively with the substitution of α for a^3 , is tested on experimental data for isoprene,

benzene, bromine, and iodine. Good quantitative agreement is obtained for the (V, N) transitions of isoprene and benzene. If the strong ultraviolet absorption of bromine and iodine solutions is regarded as the displaced (V, N) transition, the quantitative agreement is poor, although qualitatively in accordance with the theory. The weak $\lambda 2600$ system of benzene, and the visible continua of bromine and iodine, show the expected smaller $\Delta\nu$ with smaller f , although quantitative comparison with theory is prevented by the superposition of other solvent effects which become important in weak absorption bands.

INTRODUCTION

THE red shift of visible and ultraviolet electronic absorption spectra in solution from their position in the gas state has long been related to the dielectric constant or to the refractive index of the solvent. This paper will develop a theory for the solvent shift in terms of the electrostatic or polarization forces of the solvent assuming it to be a continuous dielectric medium, bearing in mind that observed solvent displacements may well be the result of the superposition of several effects of which the electrostatic effect is only one. Two methods of approach will be used, the first based on quantum theory where the absorption process is visualized as an electrical displacement within the absorbing molecule, and the second based on classical dispersion theory in terms of the forced, damped vibration of an electron bound by elastic forces. It will be seen that both methods lead essentially to the same result.

In both cases it will be assumed that the absorption process is so rapid that only the electron polarization of the surrounding solvent medium can respond to it; i.e., we shall identify the effective dielectric constant K of the solvent with n^2 , where n is its refractive index at the frequency concerned, and use K and n^2 interchangeably throughout. This assumption is obviously true in terms of the classical model of absorption, since the frequency of the vibrating electron is known to be too great to exert any orienting effect on permanent solvent dipoles. Its truth for the quantum theory model is indicated by the Franck-Condon principle, according to which the initial absorption is regarded as extremely rapid compared with nuclear motions. After the initial process, and during the relatively long life of the excited molecule, there will doubtless be time for any required re-orientation of solvent dipoles to occur, involving transfer of orientation polarization energy between solute and solvent. While this subsequent effect will be of importance in photo-chemical changes

and in re-emission by fluorescence, it is without influence on the initial "vertical" Franck-Condon absorption, where the only transfer of energy between solute and solvent is by means of electron polarization.

THEORETICAL

Quantum-Mechanical Model

If an absorption transition occurs between states with wave functions ψ_1 and ψ_2 , the electric dipole matrix element for an electronic displacement in the x direction,

$$\int \psi_1 x \psi_2 d\tau = eQ \quad (1)$$

is a measure of the absorption intensity. It will be assumed in this paper that the transition integral Q is the same for absorption in the gas state as in solution, an assumption that is justified at least for strong transitions by the considerations of Mulliken and Rieke¹ and by the recent intensity measurements of Jacobs and Platt.² The red shift of absorption in solution can now be expressed in terms of the decreased electrostatic work required to produce the dipole $\mu = eQ$ in a dielectric medium as compared with the gas, or alternatively in terms of the lower electrostatic energy of this dipole in solution.

If an electric field F acting on a molecule produces a dipole $\mu = \alpha F$, where α is the polarizability, then the work required *in vacuum* is $\mu^2/2\alpha$.³ With a naive interpretation of the dielectric constant K of the solvent, the corresponding work in solution is $\mu^2/2\alpha K$, leading to a shift of the absorption to lower frequencies

¹ R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.* **8**, 231 (1941).

² L. E. Jacobs and J. R. Platt, *J. Chem. Phys.* **16**, 1137 (1948).

³ J. C. Slater and N. H. Frank, *Introduction to Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1933), p. 550.

given by (ν in cm^{-1}):⁴

$$\Delta\nu = (\mu^2/2\alpha hc)(1-1/K). \quad (2)$$

Onsager's work⁵ has shown however that the solute dipole itself modifies the dielectric constant of the solvent in its immediate vicinity, and his treatment of the external effect of the dipole suggests that $1/K$ should be replaced by $3K/K(2K+1)$, leading to the following formula in which μ has been replaced by eQ :

$$\Delta\nu = (e^2Q^2/\alpha hc)[(K-1)/(2K+1)]. \quad (3)$$

Alternatively, if we regard the dipole as a point at the center of a spherical solute cavity of radius a , Fröhlich⁶ has shown that its interaction energy with the surrounding solvent dielectric is $-\mu R/2$, where R is Onsager's reaction field on the solute dipole due to that dipole's effect on the solvent given by⁵

$$R = (\mu/a^3)(2K-2)/(2K+1). \quad (4)$$

If the lowered absorption frequency in solution is attributed to this interaction energy, one obtains

$$\Delta\nu = (e^2Q^2/a^3hc)[(K-1)/(2K+1)], \quad (5)$$

which would be identical with Eq. (3) if $a^3 = \alpha$. It is more usual to relate α and a^3 by means of the "internal refractive index" n' of the solute molecule by $\alpha = a^3(n'^2-1)/(n'^2+2)$, where the factor involving n' is probably between $\frac{1}{3}$ and $\frac{1}{4}$.

The Classical Model

The classical dispersion equation⁷ for the vibration of an electron bound elastically to an absorbing molecule in the gas state is

$$m\ddot{x} + mg\dot{x} + \omega_0^2 mx = eF \quad (6)$$

where F represents the oscillating electric field of the light wave and is given by $F^0 \exp(i\omega t)$, g is the damping coefficient, and where the elastic restoring force term $\omega_0 = 2\pi\nu_0 c$ if ν_0 (cm^{-1}) is the frequency of maximum absorption. If the absorbing molecule is now regarded as placed in a dielectric solvent medium, F will be altered by the solvent, but the change will affect ω_0 only if the altered value of F contains a term in x . This is in fact the case, since Onsager⁵ has shown that if the solute molecule is regarded as a spherical cavity of radius a in the surrounding solvent, then the Clausius-Mosotti field of the external field F is the sum of two parts, a cavity field and a reaction field. The former is independent of the solute dipole and may be represented by F' for our present purpose. The reaction

field R however depends on the instantaneous dipole $\mu = ex$ of the solute molecule (see Eq. (4)).

If the absorption transition under consideration has the oscillator strength f , each absorbing molecule has f electrons of natural frequency ω_0 , and hence in solution each solute molecule exerts a total reaction field,

$$fR = (fex/a^3)[(2K-2)/(2K+1)]. \quad (7)$$

Equation (6) becomes

$$m\ddot{x} + mg\dot{x} + \omega_0^2 mx = e(F' + fR). \quad (8)$$

The terms in x become

$$mx \left[\omega_0^2 - \frac{e^2 f (2K-2)}{ma^3 (2K+1)} \right],$$

showing that the natural vibration frequency in solution is lowered by the amount

$$\Delta(\omega^2) = 2\omega\Delta\omega = \frac{e^2 f (2K-2)}{ma^3 (2K+1)} \quad (9)$$

which with the substitution $\omega = 2\pi\nu c$ and $K = n^2$ gives

$$\Delta\nu = \frac{e^2}{4\pi^2 c^2 m} \cdot \frac{f}{\nu a^3} \cdot \frac{n^2-1}{2n^2+1} = 7.14 \times 10^9 \frac{f}{\nu a^3} \cdot \frac{n^2-1}{2n^2+1}. \quad (10)$$

Introducing the relationship between f and Q , namely,

$$f = (8\pi^2 mc/3h)\nu Q^2$$

into Eqs. (3) and (5), we get

$$\Delta\nu = \frac{3e^2}{8\pi^2 c^2 m} \cdot \frac{f}{\nu a^3} \cdot \frac{n^2-1}{2n^2+1} = 10.71 \times 10^9 \frac{f}{\nu a^3} \cdot \frac{n^2-1}{2n^2+1} \quad (11)$$

$$\Delta\nu = \frac{3e^2}{8\pi^2 c^2 m} \cdot \frac{f}{\nu a^3} \cdot \frac{n^2-1}{2n^2+1} = 10.71 \times 10^9 \frac{f}{\nu a^3} \cdot \frac{n^2-1}{2n^2+1}, \quad (12)$$

respectively. The numerical constants are those appropriate if a and α are expressed in Å and Å³, respectively. Equations (10)–(12) are identical except for the different numerical factor in (10), and the replacement of a^3 by α in (11).

DISCUSSION

Expressions with similar dependence on n and a have been derived previously. To take some recent examples, Sheppard,⁸ in his review of the effect of the environment on the spectra of dyes, has suggested that $\Delta\nu = \text{const.}(1-1/K)$ although the experimental results are somewhat more complex than predicted by this simple formula. In a treatment designed particularly for the case of vibration spectra, Kirkwood⁹ has found $\Delta\nu$

⁴ This formula, with an incorrect numerical factor, was presented by the author at the Perth (1947) meeting of the Australian and New Zealand Association for the Advancement of Science in a paper published by title only in the Proceedings, Vol. 24, p. 107. See also N. S. Bayliss, Nature (May, 1949).

⁵ L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).

⁶ H. Fröhlich, Trans. Faraday Soc. 44, 238 (1948).

⁷ Reference 3, p. 276.

⁸ S. E. Sheppard, Rev. Mod. Phys. 14, 303 (1942).

⁹ J. G. Kirkwood, quoted by W. West and R. T. Edwards, J. Chem. Phys. 5, 14 (1937).

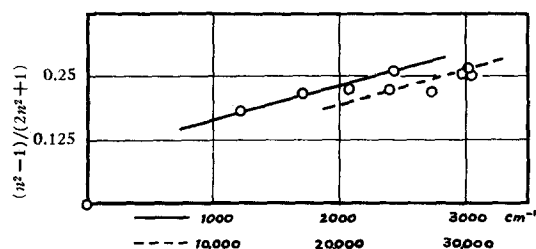


FIG. 1. Upper (full) line: Plot of $\Delta\nu$ against $(n^2-1)/(2n^2+1)$ for merocyanine in the solvents (left to right) *n*-hexane, carbon tetrachloride, benzene, carbon disulfide. Lower (broken) line: $\Delta\nu$ for ultraviolet absorption of bromine in the solvents (left to right) cyclohexane, carbon tetrachloride, benzene, chlorobenzene, toluene. Refractive index data for CCl_4 were available only in the visible; the true point for Br_2 in this solvent should be closer to the broken line. The $\Delta\nu$ scale for bromine is 10 times that for merocyanine.

$=C(K-1)/(2K+1)$, and for the model of a point dipole at the center of a sphere of radius a , his C closely resembles that of Eq. (10) without its explicit dependence on f . Sambursky and Wolfsohn¹⁰ have discussed the solvent effect on the fluorescence of anthracene in terms of Onsager's dielectric theory, and find $\Delta\nu = A\mu^2/a^3$ where A is derived from the expression for the reaction field and contains K and the internal refractive index n' .

It is believed that this is the first time the dependence of $\Delta\nu$ on the oscillator strength f has been stated explicitly, although it is implicit in the inclusion of μ for the excited state in Sambursky and Wolfsohn's expression¹⁰ and also in the treatment of the dispersion of solids and liquids by Slater and Frank.¹¹ Breit and Salant¹² put $\Delta\nu$ proportional to the absorption coefficient in the case of infra-red spectra.

When one compares the theoretical predictions with experiment, two qualifying factors must be borne in mind:

(a) Other solvent effects are almost certainly operative in addition to the electrostatic polarization effect considered here, including the solvent "cage" effect discussed by Bayliss and Rees¹³ and by Rees,¹⁴ and the electronic wave function overlap effect discussed generally by Breit and Salant.¹² The possibility of effects resulting from solvate formation must not be overlooked, although the author's opinion is that this effect, though present in certain cases, is less frequent than is commonly postulated.

(b) The absolute magnitude of the predicted $\Delta\nu$ depends very heavily on the geometry of Onsager's model of a point dipole at the center of a spherical solute molecule. Deviations from this model have, for example, a large effect on Kirkwood's constant C .⁹ Most organic molecules are far from spherical, and in the case of strong transitions, where Q may be of the order of 1A, the dipole is far from being a point relative to the size of the solute molecule.

It must also be remembered that in spite of the mass of experimental data on absorption spectra in solution, there are not many examples which combine reliable f

data with a systematic investigation of the effect of various solvents. The few typical examples considered here will serve to show the extent of the qualitative and quantitative validity of the theory, together with its limitations.

Dependence on n

The example of a merocyanine dye in the gas state and in several solvents is taken from Sheppard's review.⁸ The upper full line in Fig. 1, recalculated from Sheppard's figure, shows $\Delta\nu$ for the merocyanine ($\lambda_{\text{max}}(\text{gas}) = 4800\text{\AA}$) plotted against $(n^2-1)/(2n^2+1)$ for four solvents, n_D being taken for n in each case. The points lie satisfactorily on a straight line, which, however does not pass through the origin as it should if Eqs. (10)–(12) accounted completely for the displacement. Sheppard's plot of λ against n does pass through the origin, but the fit of his points to a straight line is less satisfactory than in Fig. 1. The lower broken curve shows $\Delta\nu$ for the strong ultraviolet absorption of bromine solutions plotted similarly. The points lie on a straight line parallel to that of the merocyanine. This case will be discussed further.

(V, N) Transitions in Isoprene and Benzene

These examples have been chosen, since there are recent measurements in both the gas and in solution, together with reliable f data. The data summarized in Table I are taken from Jacobs and Platt² in the case of isoprene, from Price and Walsh¹⁵ for the (V, N) band in benzene gas, and from Platt and Kleven's¹⁶ for benzene dissolved in *n*-heptane. Equations (10)–(12) have been used to calculate the values of a and α required by the theory, and these can now be compared with data from other experimental sources. Either of the values $a = 2.57\text{\AA}$ or $a = 2.94\text{\AA}$ is in good agreement with the known dimensions of the benzene molecule. In solid benzene, the molecules are known to pack as if the unsaturation electrons occupy an almost spherical

TABLE I. Molecular radius and polarization calculated from red frequency shifts of strong absorption bands.

	Isoprene ^a	Benzene	Bromine	Iodine
ν (gas) cm^{-1}	46500	55800 ^b	64000 ^d	56000 ^e
ν (soln.) cm^{-1}	44900	54500 ^c	34000 ^e	33600 ^b
Solvent	<i>n</i> -heptane	<i>n</i> -heptane	benzene	benzene
$\Delta\nu$ cm^{-1}	1600	1300	30000	22400
f	0.40	0.79 ^e	0.18 ^e	0.21 ^b
n (solvent)	1.46($\lambda 2250$)	1.46($\lambda 2250$)	1.61($\lambda 2900$) ^f	1.61($\lambda 2900$)
a [Eq. (10)] in \AA	2.03	2.57	0.60	0.72
a [Eq. (12)] in \AA	2.31	2.94	0.69	0.83
α [Eq. (11)] in \AA^3	12.5	25.4	0.33	0.57

^a Data from Jacobs and Platt, reference 2.

^b Price and Walsh, reference 15.

^c Platt and Kleven's, reference 16.

^d Estimated position of (V, N) transition, reference 1.

^e Bayliss, Cole, and Green (unpublished results).

^f Landolt-Börnstein, "Tabellen," HW II, p. 972.

^g (V, N) transition, see reference 1.

^h Green and Rees (unpublished results), also reference 20.

¹⁰ S. Sambursky and G. Wolfsohn, Phys. Rev. **62**, 357 (1942).

¹¹ Reference 3, p. 280.

¹² G. Breit and E. O. Salant, Phys. Rev. **36**, 871 (1930).

¹³ N. S. Bayliss and A. L. G. Rees, J. Chem. Phys. **8**, 377 (1940).

¹⁴ A. L. G. Rees, J. Chem. Phys. **8**, 429 (1940).

¹⁵ W. C. Price and A. D. Walsh, Proc. Roy. Soc. **A191**, 22 (1947).

¹⁶ J. R. Platt and H. B. Kleven's, Chem. Rev. **41**, 301 (1947).

"dome" whose radius has been shown by Mack¹⁷ to be 2.45Å. If one regards liquid benzene as consisting of spherical molecules in closest packing, the molecular radius is found to be 3.0Å. In testing Eq. (11), the difficulty arises of choosing the correct value of the polarizability α , which depends on the wave-length. It would obviously be best to calculate α for the wave-length corresponding to $\lambda(\text{max.})$, but the required refractive index is unknown. The benzene molecule is also markedly anisotropic. However the mean polarizability, presumably calculated with $n=n_D$, is 10.32.¹⁸

The isoprene molecule is more elongated, but if liquid isoprene consists of spherical molecules in closest packing, one finds $a=3.1\text{Å}$, rather greater than either of the values in Table I. On the other hand, a short extrapolation from the data of Melaven and Mack¹⁹ on collision areas of hydrocarbons suggests that the collision area of pentane (somewhat similar to isoprene) is about 20Å^2 , giving $a=2.5\text{Å}$. Furthermore, using the refractive index of isoprene in the visible region, one calculates $\alpha=10.0\text{Å}^3$ in good agreement with Table I, although as in the case of benzene it would be more satisfactory to use the refractive index in the neighborhood of the absorption band. While the agreement between theory and experiment is not as good here as in benzene, the molecule departs more widely from the spherical model. (See also following discussion of bromine and iodine.)

Ultraviolet Absorption of Bromine and Iodine Solutions

Both iodine dissolved in benzene,^{20, 21} and bromine dissolved in several solvents^{22, 23} show intense absorption ($f \approx 0.2$) near 2900Å and toward shorter wave-lengths. The respective gases absorb very weakly indeed in this region, and if the solution bands are displaced from bands that are intense in the gas, the only possible parent gas bands are the (V, N) transitions of rather greater predicted intensity¹ that lie in the vacuum ultraviolet. While the solution bands have been ascribed to other causes,* it is of interest to consider the conse-

quences of the hypothesis that they are in fact displaced (V, N) transitions. The data based on this supposition regarding $\nu(\text{max.})$ in the gas are set out in Table I. Owing to the very great postulated value of $\Delta\nu$, an average of the gas and solution ν 's has been used in each case in applying Eqs. (10)–(12).

The $\Delta\nu$ data for bromine in several solvents are plotted also in Fig. 1 (lower broken line). The points lie on a straight line which, as in merocyanine, does not pass through the origin, although it is parallel to the merocyanine line, suggesting that the solvent displacements have the same cause in both cases. It should be noted that the scale of $\Delta\nu$ for bromine in Fig. 1 is ten times as great as for merocyanine, and the much greater "spread" between the solution maxima in bromine than in merocyanine (a fact that is independent of any hypothesis about the location of the gas absorption) shows that the parent gas absorption in bromine must be much further removed from the solution spectra than in merocyanine.

The calculated values of a (Table I) are all much smaller than the actual molecular radii (e.g., 2.5Å for bromine). There is also a very great discrepancy in the polarizabilities, the ordinary experimental values being 8.0Å^3 and 11.0Å^3 for bromine and iodine, respectively. The model of a point dipole at the center of a spherical molecule may well be at fault, however. In a similar discussion by West and Edwards⁹ of the solvent displacement of the infra-red absorption of HCl, Kirkwood's formula⁹ required $a=0.62\text{Å}$ for HCl instead of the more reasonable value of 2Å. Changing the model to locate the dipole off-center was able to bring about much better agreement. A similar treatment might resolve the difficulty in the iodine and bromine cases, since the plot of $\Delta\nu$ for bromine in Fig. 1 strongly suggests that we are dealing with a large solvent displacement. The case of iodine in benzene is admittedly complex.²⁰

Weak Absorption Bands in Benzene, Bromine, and Iodine

Benzene, with its transitions of differing intensity at 1790Å ($f=0.79$), 1980Å ($f=0.1$),¹⁸ and 2600Å ($f=0.0006$),²⁴ offers the possibility of checking the theoretical dependence of $\Delta\nu$ on f by comparisons within the one molecule. Unfortunately, it is difficult to estimate $\Delta\nu$ from the published data on the 1980Å transition in the gas¹⁵ and in solution¹⁶ except that it is apparently less than for the (V, N) transition, in qualitative agreement with theory. Data for the weak system at 2600Å in the gas and in solution are quoted by Sponer,²⁵ from which $\Delta\nu$ appears to be about 300

has ascribed the UV solution bands of both bromine and iodine to solvates. The author proposes to deal further with the problem in a future publication.

²⁴ R. S. Mulliken, J. Chem. Phys. 7, 353 (1939).

²⁵ H. Sponer, Chem. Rev. 41, 281 (1947).

¹⁷ E. Mack, Jr., J. Am. Chem. Soc. 54, 2141 (1932).

¹⁸ Landolt-Börnstein, "Tabellen," Erg. Bd. III.1, p. 153.

¹⁹ R. M. Melaven and E. Mack, Jr., J. Am. Chem. Soc. 54, 888 (1932).

²⁰ J. H. Hildebrand and H. A. Benesi, J. Am. Chem. Soc. 70, 2832 (1948).

²¹ B. G. Green and A. L. G. Rees (private communication).

²² Aickin, Bayliss, and Rees, Proc. Roy. Soc. A169, 234 (1948).

²³ Bayliss, Cole, and Green (unpublished results).

* Hildebrand and Benesi (reference 20) suggest that the iodine-benzene band is the result of solvate formation involving bonding with the π -electrons of the benzene molecule. This explanation is not so plausible in the case of bromine, which shows the strong absorption not only in aromatic solvents, but also in chloroform and cyclohexane. Mulliken and Rieke regard the bromine band as an example of extreme solvent perturbation on the very weak absorption exhibited by bromine gas in the same region. If this is so, it is an example that seems to be without parallel in other solution spectra. The phenomenon is of great interest, and further work is being undertaken to obtain more quantitative data. Added in proof: In a recent paper, which the author was privileged to see in manuscript, Mulliken (J. Am. Chem. Soc., Jan. 1950)

cm^{-1} to the red (solvent not specified). Sheppard⁸ states, however, that while the shorter wave-length bands are displaced to the red (solvent unspecified), the longer wave-length bands move to the violet in solution.* From Eqs. (10)–(12), one would expect $\Delta\nu$ to be about $1/10,000$ of $\Delta\nu$ for the (V, N) transition. When the electrostatic displacement becomes so small, other effects such as that of the solvent cage^{12, 13} become predominant, and the quantitative evaluation of $\Delta\nu$ becomes impossible.

For the well-known visible continua of bromine and iodine we have $f=0.0029$ ²⁶ and $f=0.015$,²¹ respectively. If a is chosen as 0.6\AA to conform to the results for the (V, N) transition in Table I, Eq. (10) predicts $\Delta\nu=780\text{ cm}^{-1}$ for bromine in *n*-hexane. With the actual value of $a=2.5\text{\AA}$, the predicted $\Delta\nu$ is about 10 cm^{-1} . The experimental value is 100 cm^{-1} ,²⁶ while for most solvents, particularly if they are associated, the displacements

* Added in proof: K. Lauer and R. Oda (Berichte, **69**, 851 (1936)) give data for the 2600Å benzene system in 11 solvents. The displacements to the red vary from 100 to 400 cm^{-1} and are qualitatively in agreement with the refractive index law.

²⁶ Bayliss, Cole, and Green, Australian J. Sci. Research, Series A **1**, 472 (1948).

$\Delta\nu$ are to the violet ranging to 1400 cm^{-1} .²⁶ Similar experimental results obtain for iodine.²⁷ These are again cases where relatively small electrostatic displacements are superimposed by other influences such as the solvent cage effect^{12, 13, 26} which causes displacements to the violet. Other authors²⁷ have ascribed the violet shift of the iodine continuum in associated solvents to solvate formation. Whether the true explanation be solvation or caging, these and the electrostatic polarization effect are of the same order of magnitude in weak bands, and the observed displacements must be regarded as their resultant.

Subject to the complications arising out of the superposition of the other effects particularly in weak bands, the qualitative dependence of the electrostatic polarization effect on f , a (or α), and n seems to be justified by the experimental results. The quantitative agreement is good for the (V, N) transitions in isoprene and benzene, although the data do not allow one to decide which of Eq. (10)–(12) is the best. The cases of the ultraviolet absorption of bromine and iodine are much less satisfactory from the quantitative viewpoint.

²⁷ O. J. Walker, Trans. Faraday Soc. **31**, 1432 (1935).

The Vibrational Spectra of Molecules and Complex Ions in Crystals III. Ammonium Chloride and Deutero-Ammonium Chloride* †

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(Received July 11, 1949)

The infra-red spectra of thin non-scattering films of NH_4Cl and ND_4Cl were obtained at 28° , -78° and -190°C . A convenient low temperature transmission type cell usable for such films is described. No indication of fine structure due to free rotation of the NH_4^+ ions was found. Instead, evidence is presented for the existence, both above and below the λ -point, of a torsional lattice mode involving the NH_4^+ ions. The limiting frequencies of the torsional oscillations were observed at about 390 and 280 cm^{-1} for NH_4Cl and ND_4Cl , respectively. These values agree quite well with the frequencies calculated on the basis of a purely electrostatic potential function. The spectra of the low temperature modifications indicate strongly that the structures belong to the

space group T_d^1 in which the NH_4^+ ion symmetry is T_d . Of the eight observed bands, two are assigned to the triply degenerate fundamentals ν_2 and ν_4 , one to the overtone $2\nu_4$, one to the combination $\nu_2+\nu_4$ which resonates strongly with ν_3 , one to the combination of the totally symmetric mode, ν_1 , with the limiting lattice frequency, ν_6 , and two to the combinations involving the lattice torsional mode, ν_6 , i.e., $\nu_4+\nu_6$ and $\nu_2+\nu_6$. The spectra of the room temperature modifications are consistent with a structure in which the NH_4^+ ion tetrahedra are randomly distributed between the two possible equilibrium orientations in each unit cell. The λ -point transformations are probably simple order-disorder transitions between the two modifications.

I. INTRODUCTION

ALL of the simple ammonium salts have second-order phase transitions in the vicinity of -30° to -60°C , but the nature of these transitions has never

been clarified. Pauling¹ has advanced the hypothesis that these transitions mark the onset of essentially free rotation, while Frenkel,² on the other hand, has suggested that such transformations are order-disorder transitions in the orientations.

In the case of NH_4Cl a considerable amount of experimental data is available. Lawson³ has demonstrated that the evidence obtained from the measurement of

* Based in part on a thesis submitted by Edward L. Wagner in partial fulfillment of the requirements for the Ph.D. degree at Brown University (1948).

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¹ L. Pauling, Phys. Rev. **36**, 430 (1930).

² J. Frenkel, Acta Physicochimica **3**, 23 (1935).

³ A. W. Lawson, Phys. Rev. **57**, 417 (1940).