THE ROTATIONAL RAMAN EFFECT IN POLYATOMIC GASES

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Contents.

Section 1. Historical Development of Raman Effect Theory.
2. Reduction of the Dispersion Formula.
3. Calculation of Raman Intensities for the Symmetrical Rotator.
4. Raman Effect Apparatus.
5. Intensities in the Pure Rotation Band in Ammonia.
6. Rotational Raman Effect in Other Gases.
7. Summary of Results.

Plates.

Exhibit, Designed for the entertainment of the public at the Atlantic City meeting of the American Physical Society.
Plate I. The Raman Effect Apparatus.
Plate II. Thermostat.
Plate III. Rotation Spectrum of Ammonia. Microphotometer Curve of Ammonia Spectrum.
Plate IV. Diagram of Ammonia Rotation Intensities.
Plate V. Microphotometer Curves of the Rotation Bands of Ethylene and Methane, and the Vibration Band of Methane.
Plate VI. Enlargements of the Rotation Bands of Ethylene, Carbon Dioxide, and Ethane.
Plate VII. Ethane Vibration Band. Microphotometer curves of Propane.
Plate VIII. The Q-branch of Hydrogen.

Abstract.

An account is given of the relation of the theory of the Raman effect developed by Placzek to the theory based upon the Kramers Heisenberg dispersion formula. The equivalence of the two is shown in the general case.

An outline is given of the proceedure used by Prof. W.V.Houston and the writer in evaluating the integrals resulting from this theory for the intensities of the individual rotation lines for molecules of the symmetrical top class.

The results of this calculation are verified experimentally in the case of ammonia gas, using accurate photometric technique. It is shown (1) that the general intensity distribution over the pure rotation band is as predicted; (2) that the effect of the nuclear spin of the hydrogen atoms must be taken into account; (3) that the relative intensity of the R-branch lines and S-branch lines corresponds to a molecule which is nearly planar, in agreement with results from the infra red spectra. The frequencies of the rotation and vibration lines are also discussed. The line at 3219 cm^{-1} is interpreted as due to the unsymmetrical vibration of the hydrogen nuclei, not previously observed.

The rotation structure of a series of the simpler hydrocarbons, as well as carbon dioxide, has been investigated. Methane shows no pure rotation, in agreement with theory. The rotation band of acetylene has been obtained, and gives the value $23.45 \cdot 10^{-40}$gm cm^2 for the moment of inertia. Ethylene shows a structure with slight irregularities which have not been fully accounted for; the moment of inertia is found to be approximately $30.1 \cdot 10^{-40}$ gm cm^2. An interpretation is suggested for the results with ethane which yields A $38.2 \cdot 10^{-40}$ gm cm^2. The resolution in the case of carbon dioxide is entirely unambiguous, and gives A $70.2 \cdot 10^{-40}$ gm cm^2.

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Historical development
of
Raman effect theory.

Smekal's consideration(1) of the modification of the frequency of light during scattering was based upon the corpuscular description of light quanta such as is employed in discussing the Compton effect. Kramers and Heisenberg (2) showed that the same phenomenon could be predicted by the wave theory of light. Treating the atom by purely classical analysis as a multiply periodic system, they expressed its electric moment, when perturbed by the field of an incident light wave, in terms of an expansion which contained not only the frequency of the incident light, but combinations of this with the frequencies characteristic of the atom. The coefficients depended upon the contact transformation from the action and angle variables for the unperturbed system to those for the perturbed system.

At this point the transition was made to quantum theory by means of the correspondence principle. The frequencies of the multiply periodic system were replaced by those associated by the usual rule with transitions from the initial stationary state of the system to some final state. Each coefficient in the expansion became essentially a summation, over all possible intermediate states of the system, of the product of the transition probability from the initial to the intermediate state times that from the intermediate to the final state.

The essential feature of this mode of attack is the appearance in the intensity expression for each shifted line of a summation over all excited states of the system. The presence of these intermediate states therefore becomes an integral part of the physical picture of the scattering process. It is important to note that this physical picture of the process as a " double jump " rests solely upon the dispersion formula. In other words it depends upon the mathematical machinery by which the Kramers Heisenberg formula was deduced, and could not be foreseen by purely physical reasoning before the problem was translated into a mathematical form.
Needless to say the later rigorous quantum-mechanical derivations of the formula (3) do not alter this conclusion, but only substitute a new machine for the old one.

As a result of this method of derivation, the phenomenon of the Raman effect was for several years interpreted physically only through the double jump picture, and depended for its quantitative treatment entirely upon the Kramers-Heisenberg formula.

Much information was obtained from this point of view. For example, the surprising fact, pointed out by Wood,(4) that alternate rotation lines were missing in the Raman spectrum of HCl was soon explained on this basis. In order that the state p may combine with the state q in the Raman effect the double jump picture of the process requires that q may combine with some other state r in ordinary emission or absorption. To produce any appreciable intensity, there must be many levels r for which this is true, which means that they must belong mainly to excited electronic states. The Raman selection rules are therefore to be derived from the rules for band spectra. It was clearly pointed out by Ras#etti(5), Hill and Kemble,(6) and others, that this required, for diatomic molecules whose ground electronic levels were Σ states, that the rotational quantum number J must change by 0 or ±2. For molecules in a Π state, however, ΔJ might also be ± 1, since for band spectra ΔJ could then be 0 as well as ± 1. This has been confirmed by Rasetti in the case of the molecule NO.(7)

But since this method of analysis requires a knowledge of the selection rules for band spectra , it is not adaptable to polyatomic molecules, for which in general electronic transitions have not been studied; this is a serious limitation. It is true that one can make definite predictions by assuming that the electronic change does not affect the usual selection rules which are valid in the infra-red. But such a basis for theoretical predictions is hardly satisfactory.

As a matter of fact selection rules obtained in this way for rotation lines turn out in general to be correct in polyatomic molecules. The dependence of the rotational selection rules upon electronic structure, mentioned above for diatomic molecules, does not hold in general. This is because it is connected with the impossibility of defining relative to the nuclei an azimuth about the molecular axis. The coordinate associated with electronic angular momentum around this axis is therefore one of the coordinates fixing the position of the system in space. For this reason in linear molecules the component of electronic angular momentum along the axis plays the same role in selection rules as the same component of angular momentum (measured by K) due to nuclear motion in polyatomic molecules. In both cases the effect is to permit $\Delta J = \pm 1$ in the Raman effect; but when the angular momentum has no component along the axis (Σ states, or $K = 0$), ΔJ is limited to 0, ± 2. This connection between electronic and rotational motion for linear molecules may be compared to the relation between vibrational and rotational motion for linear polyatomic molecules, such as CO_2 and C_2H_2. In this case the coordinate φ, nominally a rotational coordinate, becomes associated with the vibrational motion.

On the other hand, the interaction of vibration and rotation in degenerate vibration in non linear polyatomic molecules, discussed by Teller and Tisza(8) is not the same phenomenon. Here the vibrational motions may involve angular momentum as before, but they are entirely specified by coordinates which can be defined relative to the equilibrium positions of the nuclei, and so do not encroach upon the realm of the rotational coordinates. In this case the effect of the interaction is to change the energy levels but not the rotational selection rules.

In the matter of predicting vibrational selection rules for the Raman effect from the double jump point of view more difficulty is experienced. In band spectra all values of ΔV occur; for a given electronic jump the Franck-Condon principle may be used to distinguish between the probable and improbable vibrational transitions. Van Vleck(9) points out the difficulty that this produces: in certain cases very large changes in V are favored as well as small ones; if V is large in the first jump and small in the second, (or vice versa) the net vibrational change is observed in the Raman effect will be large; however large changes are not observed.

The answer which Van Vleck gives is that the large values of Δ V require a large change in phase in the vibrational motion sometimes as much as π . Therefore for any given Δ V, the contributions to the intensity from intermediate states with different vibrational quantum numbers will be out of phase. For small Δ V the phase disagreement will be slight, so that the contributions of the various upper states will combine more effectively.

A qualitative explanation of the absence of large changes in V. can also be based upon probability rather than phase difference.

Let us denote various vibrational levels of the electronic ground state by V_n, and of the intermediate excited state by V'_n ; consider only molecules initially in the state V_1 . The Franck-Condon principle now determines two most probable intermediate states, V'_1 and V'_2 ; From V'_1 the molecule is most likely to return to either V_1 or V_2; from V'_2 it is most likely to return to either V_1 or V_3, where V_2 and V_3 are determined by the same principle. Assuming, as a simplifying approximation, equal probabilities for the two choices in each case, one finds that one half the Raman transitions end at V_1 and one quarter at each of V_2 and V_3. This in itself would not be very significant. But one must remember that all excited electronic states must be considered, and that in general for each one the corresponding values of V_2 and V_3 will be different. So we have half of all the Raman transitions ending at V_1, with the other half splitting their vote among all other vibrational states. In this analysis

V_n must of course be thought of as including a number of states on each side of V_n itself. Hence the transition $V_1 \rightarrow V_1$ really means only that ΔV is small, not that $\Delta V = 0$. No attempt has been made to make this treatment rigorous. Neither it nor that of Van Vleck, outlined above, is intended as more than a helpful qualitative interpretation of the absence from the Raman effect of large changes in vibration.

To give definite information it is necessary to turn from the rather unfruitful double jump picture itself to the corresponding mathematical expression of the process, - the dispersion formula. Van Vleck simplifies this formula, by methods to which we shall return presently, sufficiently to explain the absence of large vibrational transitions. The theory is again, however, unable to make further progress in the polyatomic case; for example, such questions as which normal modes of vibration are permitted in the Raman effect cannot be answered. This failure of the theory at first led to much confusion in the correlation of Raman effect data with that of the infra-red.

The difficulties and sharp limitations that have just been described become readily understandable when the foundations upon which the theory is laid are examined.

One of the striking characteristics of many molecular problems is the extent to which the vibration and rotation of the nuclei can be discussed independently of the electronic functions. For example in the theory of infra-red spectra very little need be said about electrons. With the early treatment of Raman effect by the dispersion formula and the resulting " double jump " picture of the process this was definitely not the case. Because the intermediate state was an excited electronic state, it was continually necessary to discuss electronic functions, states, and selection rules. No possibility of avoiding this was apparent, in spite of the very suggestive fact that in the Raman effect as actually observed no net change of electronic state takes place--with one lone exception.(7)

In order to understand this failure of the theory to take advantage-- as is done in the infra-red--of the particular characteristics of the problem, it is helpful to notice the following point with regard to the Kramers-Heisenberg treatment. These authors use the word " atom " rather than the word " molecule ". This is quite natural, and is no limitation, of course, upon the applicability of their results,since the type of functions and energy levels that appear in the final formulae have only to be generalized to include nuclear as well as electronic motion. But it is significant that the mathematical machinery used in the derivation is designed primarily for the case of electronic motions alone. As a result, the final expression, generalized to include nuclear motions, is in a form which cannot readily take account of particular properties which are characteristic of the molecular system.

This difficulty may be remedied in either of two ways. One of these--actually the second to be developed-- is to agree at the start that only molecules and not atoms are to be discussed; a distinct theoretical procedure can then be developed in which the properties peculiar to molecules are made use of to simplify the problem before it is translated into mathematical form. This method entirely avoids the complex superstructure of excited states which destroyed the usefulness of the more general dispersion formula. It gives a simple and direct physical picture of the Raman effect without use of the double jump idea. Placzek has put the theory of the Raman effect on a new basis by his thorough development of this point of view.

The other method accepts as a starting point the dispersion formula in its usual form-- which was originally derived specially for application to atoms and then generalized to include molecules. The properties peculiar to the molecular case are then employed, and by their means the formula is once more specialized so that it is no longer applicable to atoms, but is well suited to the study of molecules. Both these methods rest upon the same basis--namely, the recognition and application of the particular characteristics of the problems at hand. In one case the simplification is applied before the problem is put in mathematical form; in the other, it is introduced afterwards.

The second method, the specialization of the general dispersion formula, has been carried through by Manneback(10) for the case of diatomic molecules. He followed the same course developed independently by Van Vleck, referred to above, but pursued it much further. This depends fundamentally upon the separability of the wave functions into electronic, vibrational, and rotational parts, and upon the large difference in magnitude of the energies associated with these three types of motion. It proves possible to carry out the summation over the intermediate states so far as the nuclear quantum numbers are concerned. The remaining summation involves the electronic states; but it is the same for all rotation lines of a band, and need not be evaluated explicitly. The whole effect of the electronic functions is contained in this summation, which can, so to speak, be represented by a letter and dismissed from one's mind. Thus all the problems of intermediate excited electronic states are solved, and one has left only integrals over initial and final states of the vibrational and rotational functions. These integrals are carried out by Manneback, giving intensity distribution and polarization of the rotational bands for diatomic molecules.

Manneback mentions, almost in passing, that the complicated summation which we represented above by a letter is actually the polarizability of the molecule for the special case of fixed nuclei. This is a very important contribution to the Raman effect theory; for it leads us back from the tangled web of the dispersion formula and its double jump to the simple physical concept of polarizability. Manneback's chief interest is in the resulting simplification of the formulae, and he does not point out the physical picture of the Raman effect which is suggested. In fact, from the somewhat involved nomenclature that has to be employed, one is rather led to believe that this sudden popping up of so simple a quantity as the polarizability of a " rigid " molecule is largely a matter of coincidence. This, of course, is decidedly not the case.

On the contrary it suggests that such a quantity should have been employed from the start; and that it might have replaced the complications of the dispersion formula all the way through, instead of appearing only at the end. Placzek's analysis, referred to above, accomplishes just this, and, as one would expect, leads to just the expressions derived by Manneback by the longer winded method.

Kramers and Heisenberg expressed the electric moment as an expansion containing all the frequencies of the system, including those of the electronic motion. Once this mathematical step is taken, it is difficult to separate the electronic part from the rest. Placzek, on the other hand, writes the electric moment as a function of nuclear coordinates only, neglecting the high frequency variation due to the electronic motions. Thus only the nuclear functions are involved when the problem is translated into the mathematical language of quantum mechanics.

His procedure may be justified in two ways. That which he employs is an appeal over the head of the dispersion formula to the physical principles at the basis of the scattering process. The second is an appeal directly to the dispersion formula, which, when simplified by such a process as Manneback uses, gives the same results. But Manneback's derivation was limited to the special case of diatomic molecules. It does not appear to have been appreciated that the same methods can equally well be applied to the general polyatomic case. For example Placzek says,(11, II) " This method is fairly troublesome and can be successfully applied in the case of diatomic molecules only, as the knowledge of the properties of the excited electronic states necessary for carrying out the process is not available for polyvalent molecules." In order to make clear just what assumptions the process requires, we shall now carry through for the general case the derivation by means of the dispersion formula of the expressions at which Placzek arrives by " physical " reasoning.

Reduction of the Dispersion Formula.

In this section we shall follow closely the method used by Van Vleck(9) and more extensively by Mannaback(10) for transforming the dispersion formula into a form adapted to the discussion of diatomic molecules. It will be shown, however, that this analysis can be applied in the general as well as in the diatomic case. In this way it will be possible to justify from the quantum mechanical point of view the intensity expressions which Placzek has derived by the correspondence principle from what we may call the " polarizability picture " of the Raman effect process.

When light of frequency ν_0 falls upon a gas, the energy scattered per second per molecule, with change of frequency corresponding to a transition of the molecule from the state p to the state q, is given by

$$\mathcal{U}(pq) = \frac{64\pi^4}{3c^3} \left| \bar{\mathfrak{M}}(pq) \right|^2 \left[\nu(pq) + \nu_0 \right]^4$$

M(pq) is the matrix element of the electric moment induced in the molecule by the field $\bar{\mathcal{E}}$ of the incident light.

It will be sufficient for our present purpose to discuss only the X component of the moment induced by light plane polarized in the Z direction, since the result we shall prove can be extended at once to the other components. If the positive and negative dispersion terms are written in one summation, the general

Kramers Heisenberg formula then gives

$$M_X(pq) = \frac{E_Z}{2h}\sum_r \left\{ \frac{M^0_X(pr)\, M^0_Z(rq)}{\nu_{rq} + \nu_0} + \frac{M^0_X(rq)\, M^0_Z(pr)}{\nu_{rq} - \nu_0} \right\} \qquad (1)$$

p, r, q, represent all the quantum numbers of the system in the initial, " intermediate " , and final states, respectively. The quantum numbers r run over all states of the system, including the continuous region of excited levels. $M^0_X(pr)$ is the p→r matrix element of the X component of the electric moment for the system when not perturbed by any external field. It is therefore given by

$$M^0_X(pr) = \int \psi_p^* \, P_X \, \psi_r \, d\tau \qquad (2)$$

where ψ is the complete wave ~~of~~ function of the unperturbed system, including nuclear as well as electronic motion; and P_X is the X component of the electric moment of the molecule. Specific expressions for P_X will be introduced later.

It is already assumed in (1) that ν_0 does not coincide with a characteristic frequency of the molecule. We shall further limit the generality of (1), but only in respects which do not prevent its application to the Raman effect as ordinarily observed. That is, we assume excitation with visible or near ultra-violet light, and consider only those Raman transitions which do not involve changes in the electronic energy of the molecules.

The reduction of formula (1) depends fundamentally upon the separability of the wave functions ψ into electronic, vibrational, and rotational parts. It involves also, as was pointed out in the last section, the notion of the electronic polarizability of the molecule when the nuclei are held fixed. In developing the first of these two points we depend upon the treament of Born and Oppenheimer$^{(12)}$. In order to make more definite the degree of approximation that is employed we shall sketch as briefly as possible the essentials of their method as well as the result.

Let x_i, y_i, z_i be the cartesian coordinates of the electrons (denoted collectively by x) with respect to axes X,Y,Z fixed in space. Relative to the same axes the coordinates of the N nuclei are X_i, Y_i, Z_i (denoted also as X). These can however be expressed in terms of 3N-6 variables $\xi_i(X)$ which depend only upon the relative separation of the nuclei, and six variables $\theta_i(X)$. Three of the latter locate the center of gravity of the system in space; the dependence of the solution on them is trivial, and need not be considered. The remaining three give the orientation of the molecule in space, and may be taken as the Eulerian angles θ, φ, ψ; we shall speak of these as θ.

The Hamiltonian is now written in two parts, where

H_0 represents

$$H = H_0 + \varkappa^4 H_1$$

Ho represents the total potential energy together with the electronic kinetic energy. $\varkappa^4 H_1$, gives the kinetic energy of the nuclei. $\varkappa$ is the small quantity $(m/M)^{\frac{1}{4}}$, where m is the mass of an electron, and M an average of the nuclear masses.

The variables ξ can also be written $\xi + \kappa\zeta$, where $\kappa\zeta$ denotes small deviations of the nuclei from the positions ξ, which may, in particular, give their positions of equilibrium.

The wave equation for the system is

$$\left(H_0 + \kappa^4 H_1 - W\right)\psi = 0 \tag{3}$$

Each of the quantities H_0, H_1, W, ψ is now expanded in a power series in terms of the small quantity κ.

$$\psi = \psi^0 + \kappa\psi^{(1)} + \kappa^2\psi^{(2)} + \cdots\cdot \quad , \text{etc.} \tag{4}$$

Setting equal to zero the coefficients of successive powers of κ, one obtains Naherungsgleichungen, which may be solved successively.

The zero order equation $(\kappa = 0)$ is

$$\left(H_0^0 - W^0\right)\psi^0 = 0 \tag{5}$$

This is just the wave equation for the electronic motion when the nuclei are held fixed at the positions ξ.
Since H_0 contains the potential energy, which depends upon ξ, ϑ as well as upon x, the solution will depend parametrically upon ξ, ϑ. Let $\varphi^0(x; \xi, \vartheta)$ be a solution of (5) ; it remains a solution if multiplied by an arbitrary function of ζ and ϑ alone, since ξ and ϑ appear in (5) only as parameters. Therefore we write the zero order solution as

$$\psi^0 = \chi_n(\zeta, \vartheta)\,\varphi_n^0(x; \xi\vartheta) \tag{6}$$

It proves necessary to introduce $\chi_n(\xi,\vartheta)$ in order that the higher order equations may be solved. Being a function of ξ and ϑ alone, it is to be considered a constant in this approximation, which represents fixed nuclei. This function remains arbitrary in the zero approximation, and may be <u>set</u> equal to unity.

The approximation we shall use includes only the first term in the expansion (4) for ψ. But ψ^0 is not completely determined by (5) since in the zero order approximation $\chi_n(\xi,\vartheta)$ is still arbitrary. Born and Oppenheimer show that in the solution of the second order Naherungsgleichung $\chi_n(\xi\vartheta)$ is partially determined, so that

$$\chi_{ns}(\xi,\vartheta) = \rho_{ns}(\vartheta)\,\sigma^0_{ns}(\xi)$$

Here $\sigma^0_{ns}(\xi)$ is the eigenfunction of the nuclear vibrational motion, while $\rho_{ns}(\vartheta)$ is again an arbitrary function. In the solution of the fourth order equation, ρ_{ns} is determined as $\rho^0_{ns}(\vartheta)$ and is the eigenfunction of the rotational motion. Thus it is necessary to go to the fourth order equation to determine ψ^0 completely. We obtain

$$\psi^0_{nsr}(x,\xi,\vartheta) = \varphi^0_n(x,\xi,\vartheta)\,\sigma^0_{ns}(\xi)\,\rho^0_{nsr}(\vartheta) \tag{7}$$

At the same time the energy is determined as far as the fourth order term in its expansion.

$$W_{nsr} = W^0_n + \kappa^2 W^{(2)}_{ns} + \kappa^4 W^{(4)}_{nsr} \tag{8}$$

$W^{(1)}$ and $W^{(3)}$ are both zero. Here the successive terms represent the electronic, the vibrational, and the rotational parts of the energy. Interaction terms enter only when we go to higher approximations, and we shall not consider them. This degree of approximation corresponds to that employed by Manneback for diatomic molecules.

We may now proceed to the discussion of the polarizability of the" rigid " molecule. Let us substitute the zero order functions (6) in the integrals of (1), and use the corresponding zero order energy values W_n^0 to calculate ν_{pr} and ν_{qr} in the denominators. We denote the quantum numbers of the initial state p by n', s', r'; of the intermediate state r by n,s,r; and of the final state q by n" s"r". Since the nuclei are held fixed, we may choose their positions in such a way that the axes x,y,z coincide with the fixed axes X,Y,Z. We may then denote the various components equally well by small as by large subscripts. In this case the dependence upon the angles θ becomes trivial and will be omitted. We then obtain from (1)

$$\mathfrak{M}_X(n',n'') = \frac{E_Z}{2h}\sum\left\{\frac{m_x(n'n)\,m_z(nn'')}{\nu_{nn''}+\nu_0} + \frac{m_x(nn'')\,m_z(n'n)}{\nu_{nn'}-\nu_0}\right\} \qquad (9$$

where

$$m_x^0(n',n) = \int \varphi_{n'}^{0*}(x;\xi)\;p_x\;\varphi_n^0(x;\xi)\,dx \qquad (1$$

and

$$p_x = \sum e x_i$$

The part of the electric moment is due to the nuclei is omitted, since for fixed nuclei it is constant. It could therefore contribute to the value of the integral only if $n' = n = n''$; but in this case the two terms in the bracket of (2) are equal and opposite.

We now set $n'' = n' = n_0$ where n_0 represents the normal electronic state. Then (9) gives the X component of the electric moment which is induced by the incident light in the molecule when the latter is in the normal electronic state, and when the nuclei are held fixed. We may therefore write

$$M_X(n_0, n_0) = E_Z\,\alpha_{zx}(\nu_0, \xi) \tag{11}$$

where $\alpha_{zx}(\nu_0, \xi)$ represents the "zx " component of the polarizability α of the rigid molecule for the frequency ν_0 . It is seen to be independent of the electronic coordinates. It does, however, depend parametrically upon the particular positions at which the nuclei are held fixed. This results from the parametric dependence of φ_n^0 upon ξ , which is carried over into (11). Our object is now to show that when the nuclei are no longer held fixed, but are allowed to vibrate and rotate, the electric moment (1) can be expressed, to a certain degree of approximation, in a form which depends upon the electronic functions only through the appearance of the electronic polarizability α.

It is seen from (8) that the electronic energies are of a higher order of magnitude than the vibrational; therefore we may consider that all the molecules are initially in the ground electronic state. Since we shall limit ourselves to Raman transitions in which no change of electronic energy takes place, the final state will also belong to the ground electronic level. Therefore

$$n' = n'' = n_0 \tag{12}$$

In case the ground level is degenerate, it will be necessary to sum over all the degenerate states, both initial and final (in addition to the sum over all excited electronic states already included in (1)). This will also be true in equation (9). The reasoning employed will not be affected by this summation, and for simplicity it will not be written explicitly.

In the denominator in (1) is the expression $\nu_{rp}+\nu_0$ In view of (12) and the expression for W in (11), this becomes

$$\nu_{nn_0} + \nu_{ss'} + \nu_{rr'} + \nu_0$$

If now we consider only visible or ultra-violet incident light, both $\nu_{ss'}$ and $\nu_{rr'}$ are negligible beside ν_0, so that the two denominators become $\nu_{nn_0}+\nu_0$ and $\nu_{nn_0}-\nu_0$. This elimination of the energy of vibration and rotation from the denominators is essential in order that we may presently carry out of the summations over s and r.

In the summation over n, the only terms of significance will be those for which the denominator is small. This will never be true for the first term in the bracket, since the molecules are initially in the ground electronic state, so that ν_{nn_0} cannot be negative. It will be true for the second term only if ν_{nn_0} is large. Therefore we need consider in the summation only terms which represent an electronically excited intermediate level. That is, $n \neq n_0$.

From the mechanical model point of view, $n \neq n_0$ because the nuclei will not be materially affected by a field which alternates as rapidly as that of the incident light, so that the polarizability may be considered as due wholly to the electrons. In other words, terms in the polarizability which represent no electronic transition may be neglected.

We now turn to the numerators in (1), of which a typical term is given by (2). If we introduce the separated form (7) of the wave functions, and the condition $n' = n'' = n_0 \neq n$, this becomes

$$M_X(p,r) = \int \varphi^{0*}_{n_0}(x;\xi\theta)\,\sigma^{0*}_{n_0 s'}(\xi)\,\rho^{0*}_{r'}(\theta)\;P_X(x,\xi,\theta)\,\varphi^{0}_{n}(x,\xi\theta)\,\sigma^{0}_{ns}(\xi)\,\rho^{0}_{r}(\theta)\,d\tau \qquad (13)$$

The dependence of ρ^0_r upon the electronic and vibrational quantum numbers n and s is in general very slight and has been dropped. It will be seen that its conclusion does not affect the reasoning, but would only complicate the presentation.

It must be kept in mind that the electric moment of which P_X is one component arises from the properties of the molecule alone, and has nothing to do with polarizability or perturbing fields. We must have P expressed in the same coordinates that appear in ψ. In order to take full advantage of the separated form (7) of the wave functions, it will be necessary also to have P_X in a form in which the dependence upon the various coordinates is similarly separated.

Let p_x, p_y, p_z be the components of the electric moment along axes of coordinates x,y,z fixed relative to the nuclei, and related to the axes X,Y,Z fixed in space by the Eulerian angles ϑ, φ, ψ. Then

$$P_X = p_x \cos(xX) + p_y \cos(yX) + p_z \cos(zX)$$

where cos(xX), etc., are functions of ϑ, φ and ψ alone; p_x, etc., are independent of these angles, but depend upon both x'_i, y'_i, z'_i, the coordinates of the electrons, and ξ_i, the coordinates of the nuclei. (The primes indicate electronic coordinates measured in the moving system x, y, z. The coordinates first introduced above were measured relative to X,Y, Z.) This dependence will be of the form

$$p_x = \sum_{i=1}^{3N-6} c_{xi} \xi_i + \sum_{j=1}^{n} e x'_j \qquad (15)$$

where the summations extend over N nuclei and n electrons. If the normal coordinates of the vibrational motion are taken for the coordinates ξ_i, then each c_{xi} gives the x component of the electric moment due to unit displacement of the i'th normal coordinate.

When the integration in (13) over the electronic coordinates is carried out, since $n_0 \neq n$, it is clear from orthogonality that the first summation in (9), which depends only on the nuclear coordinates, does not contribute to the value of the integral. Therefore, only the dependence of p on the electronic coordinates needs to be considered. We shall continue to write p_x, remembering that the first summation has been dropped out.

It might be claimed on similar grounds that upon integration over the vibrational (or nuclear) coordinates the contribution of the second summation in (11) would also vanish, except for the case of no change of vibrational state during scattering. Thus vibrational Raman lines would be entirely forbidden . This would be true were it not for the parametric dependence of the electronic functions $\varphi^o_n(xyz;\xi)$ upon ξ , which must be included for just this reason. It is therefore evident at this point that vibrational selection rules will be determined fundamentally by the dependence of the electronic functions upon the normal coordinates of the vibration.

Equation (13) may now be written, using (14), as the sum of three terms, of which the second is

$$\int \sigma^{o*}_{n_o s'} \, \rho^{o*}_{r'} \, m^o_y(\xi)_{n_o n} \cos(yX) \, \sigma^o_{ns} \, \rho^o_r \, d\xi \, d\theta \qquad (16)$$

where we have substituted

$$m^o_y(\xi)_{n_o n} = \int \varphi^{o*}_{n_o}(x';\xi) \, p_y(x') \, \varphi^o_n(x';\xi) \, dx' \qquad (17)$$

It is to be noted that when the primed electronic coordinates are used, φ^o_n no longer depends upon the orientation of the molecule in space.

$m_y^0(\xi)_{n_0 n}$ is the $n_0 \rightarrow n$ matrix element of the y component of the electric moment of the molecule when the nuclei are held fixed at the positions ξ . When the three terms of which M_x (pr) is composed are substituted in the products in (1), these each give nine terms. We shall write out only a typical one of these, employing the usual matrix notation.

$$\big(\cos(xZ)\big)(r',r)\ \big(\cos(yZ)\big)(r,r'')$$
$$\big(m^0_x(\xi)_{n_0 n}\big)(s'_{n_0}, s_n)\ \big(m^0_y(\xi)_{n n_0}\big)(s_n, s''_{n_0}) \qquad (18)$$

We may break up the summation in (1) into nine sums, each involving one expression of the type (18). The denominators in (1) have been shown independent of s and r. The sum over r is straightforward, from the usual law of matrix multiplication, and gives $\big(\cos(xZ)\ \cos(yZ)\big)$ (r',r"). The sum over s is carried out only a little less easily.

The dependence of the vibrational integral upon the electronic states is indicated in (18) by the use of subscripts on the vibrational quantum numbers. Because of this dependence these integrals are so-called " hybrid " matrix elements. The usual matrix elelments of a function $f(\xi)$ may be defined as the coefficients in the expansion of $f(\xi)\ \varphi_s(\xi)$ in terms of all the members of the complete set of orthogonal normalized functions

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If $f(\xi)\varphi_s(\xi)$ is expanded in terms a different set of functions $\psi_r(\xi)$, the coefficients are hybrid matrix elements. In our case the two sets of functions are the vibrational functions $\sigma_{ns}(\xi)$ for two different values of n. The multiplication law for such hybrid matrices is well known. It is derived, for example, by Van Vleck in connection with just this problem. (9) He showed in general that

$$\sum_s (f)(s'_{n_1}, s_{n_2})(g)(s_{n_2}, s''_{n_3}) = (fg)(s'_{n_1}, s''_{n_3}) \qquad (19)$$

We apply this to the summation of (18) over s, and obtain

$$\left(\cos(xZ)\cos(yX)\right)(r', r'')\left(m_x^0(\xi)_{n_0 n}\, m_y^0(\xi)_{n n_0}\right)(s'_{n_0}, s''_{n_0}) \qquad (20)$$

Since in our case $n_1 = n_3$, we obtain not a hybrid but an ordinary matrix element. Only the vibrational function for the normal electronic level are involved, and we shall drop the subscripts from s' and s". The summation over n cannot be carried out in a similar way because of the denominators.

One of the nine sums over n to which (1) has been reduced may now be written out in full.

$$E_Z \cdot \left(\cos(xZ)\cos(yX)\right)(r', r'')$$
$$\left(\frac{1}{2h}\sum\left\{\frac{m^0_x(\xi)_{n_0 n}\, m^0_x(\xi)_{n n_0}}{\nu_{n n_0} + \nu_0} + \frac{m^0_x(\xi)_{n n_0}\, m^0_y(\xi)_{n_0 n}}{\nu_{n n_0} - \nu_0}\right\}\right)(s', s'') \qquad (21)$$

The summation here becomes identical with that in equation (9) when in (9) n' is set equal to n" and X, Z are replaced by x,y. Therefore by (11) we can write (21), combining the rotation and vibration integrals, as

$$E_Z \cdot \left(\alpha_{xy}(\nu_0, \xi)\ \cos(x'Z)-\cos(yX)\right)(s'r', s''r'')$$

The quantity $\alpha_{xy}(\nu_0\xi)\cos(xZ)\cos(yX)$ is just that part of the polarizability component α_{ZX} which arises from α_{xy} when we transform the polarizability from the axes x,y,z to the fixed axes X,Y,Z. When the nine sums into which (1) was broken up are ressembled, it is found that they give just the nine terms of α_{ZX}. We therefore obtain finally, writing (1) in full, for the X component of the electric moment of the molecule produced by the Z component of the incident light, and associated with the Raman transition from the state n_0 s' r' to the state n_0, s", r", the following,

$$M_X(s'r', s''r'') = E_Z \cdot \left(\alpha_{ZX}(\nu_0; \xi\theta)\right)(s'r's''r'') \tag{23}$$

This is a matrix element involving only the vibrational and rotational functions for the ground electronic state. The intermediate states no longer appear explicitly, their effect being entirely contained in α, which, however, is a function only of the exciting frequency and of the nuclear coordinates. The simplicity and directness of this expression are in very sharp contrast to the unwieldy but more rigorous and general character of equation (1).

Equation (23) is just the expression which Placzek has derived from physical principles; his results have therefore been shown to be in accordance with the dispersion formula in the general as well as in the diatomic case.

Calculation of Raman Intensities for the Symmetrical Rotator.

We shall now turn to the actual evaluation of the intensities of the various rotation lines for molecules of the symmetrical top class. The work described in this section was principally carried out by Prof. W.V. Houston, the writer's share being a small one. The summary of the process is, however, included here for completeness and for future reference. Since the work was done a paper has appeared by Placzek and Teller (11) in which the subject is treated very thoroughly. Their intensities agree with ours, but the methods of computation and presentation are different. It is hoped that the following account, being less complete than theirs, may also be helpful in clarifying the fundamental ideas. We consider a light wave of frequency ν_0 incident along the positive X axis and polarized in the Z direction. The electric moment of the molecule may be written

$$
\begin{aligned}
\bar{M} &= \bar{i}\, M_X + \bar{j}\, M_Y + \bar{k}\, M_Z \\
&= (\bar{i}\,\alpha_{ZX} + \bar{j}\,\alpha_{Z\bar{Y}} + \bar{k}\,\alpha_{ZZ})\,\mathcal{E}_Z\, e^{2\pi i \nu_0 t}
\end{aligned}
$$

where $\alpha_{\underline{\overline{XX}}}$, etc. are the components of the tensor of polarizability referred to the fixed coordinate axes.

The matrix elements of the electric moment, formed with the wave functions of the system including their time dependence, give both the intensity and the frequency of the scattered light.

That is, the intensity of the Z component of light acattered in conjunction with a transition of the molecule from the state p to the state q, is proportional to the square of

$$(m_z)_q^p = \int \psi_q^* e^{-\frac{2\pi i}{h}(E_q t + \varphi_q)} \alpha_{zz} \mathcal{E} e^{2\pi i \nu_0 t} \psi_p e^{\frac{2\pi i}{h}(E_p t + \varphi_p)} d\tau$$

$$= \mathcal{E} e^{2\pi i(\nu_0 + \nu_{pq})t + \varphi_{pq}} \int \psi_q^* \alpha_{zz} \psi_p \, d\tau$$

where $\nu_{pq} = \frac{E_p - E_q}{h}$ and $\varphi_{pq} = \frac{2\pi i}{h}(\varphi_p - \varphi_q)$

This gives for the scattered light the frequency $\nu = \nu_0 + \nu_{pq}$, where ν_{pq} may be either positive or negative, depending upon whether the molecule has more or less energy in the initial state than in the final state. These two cases lead to the anti-Stokes and Stokes lines, respectively. The presence of φ_{pq} in the exponential shows that the scattered light is incoherent if $p \neq q$. In the case $\nu_{pq} \neq 0$ this is obvious from the start, since two vibrations of different frequency cannot be related in phase. But if there is degeneracy, so that even when $p \neq q$ we may have $\nu_{pq} \neq 0$, it is necessary to resort to a treatment like (2) to distinguish between the coherent $(p = q)$ and incoherent $(p \neq q)$ parts of the unshifted line.

According to Placzek's theory, and also, as we saw in section 2, according to the dispersion formula, the eigenfunctions in(2) include only the nuclear motion of the molecule, and are functions of the normal coordinates ξ_i of the vibration and of the angles ϑ, φ, ψ. If we omit the exponential, (2) therefore becomes

$$(M_z)^{vr}_{v'r'} = \mathcal{E}\int \sigma_{v'}(\xi)\varrho_{r'}(\vartheta\varphi\psi)\,\alpha_{zz}\,\sigma_v(\xi)\varrho_r(\vartheta\varphi\psi)\,d\tau \qquad (3)$$

In order to evaluate this integral we must investigate the dependence of α_{zz} upon the coordinates $\xi, \vartheta, \varphi, \psi$.

Let α_{ik} be the components of the tensor of polarizability referred to the principal axes of inertia of the molecule. In many cases these will be the principal axes of the polarizability. These principal axes of inertia will be independent of the vibrations of the molecule to the extent to which the rotation and vibration may be considered separately, which is the approximation which we shall use. Since the binding of the electrons depends intimately upon the distance between the nuclei, the components of the tensor α_{ik} will be functions of the normal coordinates. This dependence may be expressed by means of a Taylor expansion, giving the expression used by Placzek.

$$\alpha_{ik} = \alpha^0_{ik} + \sum \left(\frac{\partial\alpha_{ik}}{\partial\xi_l}\right)_0 \xi_l + \frac{1}{2}\sum_{l,n}\left(\frac{\partial^2\alpha_{ik}}{\partial\xi_l\,\partial\xi_n}\right)_0 \xi_l\xi_n + \cdots \qquad (4)$$

The transformation from the principal axes of inertia, x,y,z, to the fixed axes X,Y,Z may be expressed in terms of the Eulerian angles $\vartheta\ \varphi\ \psi$. The coefficients of the transformation are given in the following table.

	x	y	z
X	$\cos\psi\cos\varphi$ $-\sin\psi\sin\varphi\cos\vartheta$	$\cos\psi\sin\varphi$ $+\sin\psi\cos\vartheta\cos\varphi$	$\sin\psi\sin\vartheta$
Y	$-\sin\psi\cos\varphi$ $-\cos\psi\sin\varphi\cos\vartheta$	$-\sin\psi\sin\varphi$ $+\cos\psi\cos\varphi\cos\vartheta$	$\cos\psi\sin\vartheta$
Z	$\sin\vartheta\sin\varphi$	$-\sin\vartheta\cos\varphi$	$\cos\vartheta$

In case the principal axes of the tensor of polarizability α coincide with the principal axes of inertia, the same angles may be used to transform the polarizability to the fixed axes. Moreover, for this case the coordinates x,y,z, will coincide with the principal axes of the polarizability, so that only the diagonal components $\alpha_{xx}\ \alpha_{yy}\ \alpha_{zz}$ will be different from zero. Relative to the fixed axes, the components of the polarizability will then be

$$\begin{aligned}
\alpha_{ZX} &= (\cos\psi\sin\vartheta\cos\varphi\sin\varphi - \sin\psi\cos\vartheta\sin\vartheta\sin^2\varphi)\left\{\alpha_{xx} + \sum_l \left(\frac{\partial\alpha_{xx}}{\partial\xi_l}\right)_0 + \cdots\right\} \\
&\quad -(\cos\psi\sin\vartheta\cos\varphi\sin\varphi + \sin\psi\cos\vartheta\sin\vartheta\cos^2\varphi)\left\{\alpha^\circ_{yy} + \sum_l \left(\frac{\partial\alpha_{yy}}{\partial\xi_l}\right)_0 + \cdots\right\} \\
&\quad + \sin\psi\cos\vartheta\sin\vartheta\left\{\alpha^\circ_{zz} + \sum_l \left(\frac{\partial\alpha_{zz}}{\partial\xi_l}\right)_0 + \cdots\right\} \\
\alpha_{ZY} &= -(\sin\psi\sin\vartheta\cos\varphi\sin\varphi + \cos\psi\sin\vartheta\cos\vartheta\sin^2\varphi)\left\{\alpha^\circ_{xx} + \cdots\right\} \\
&\quad +(\sin\psi\sin\vartheta\cos\varphi\sin\varphi - \cos\psi\sin\vartheta\cos\vartheta\cos^2\varphi)\left\{\alpha^\circ_{yy} + \cdots\right\} \\
&\quad + \cos\psi\sin\vartheta\cos\vartheta\left\{\alpha^\circ_{zz} + \cdots\right\} \\
\alpha_{ZZ} &= \sin^2\vartheta\sin^2\varphi\left\{\alpha^\circ_{xx} + \cdots\right\} + \sin^2\vartheta\cos^2\varphi\left\{\alpha^\circ_{yy} + \cdots\right\} \\
&\quad + \cos^2\vartheta\left\{\alpha^\circ_{zz} + \cdots\right\}
\end{aligned} \tag{6}$$

These expressions in (3) give the three components of the electric moment.

The vibrational part of the wave functions in sufficient approximation is a product of the usual solutions of the harmonic oscillator, each involving a quantum number V_ℓ , and each depending upon one of the normal coordinates of the vibrational motion ξ_ℓ ,which have already been introduced in the expansion for α . The rotational functions depend upon the Eulerian angles ϑ, φ, ψ , also introduced above. The integrations over the vibrational and rotational coordinates in (4) may be performed separately. Upon integration over the vibrational coordinates, due to the well known properties of the eigenfunctions of the harmonic oscillator, the terms in α which are independent of the normal coordinates (see equations (6)) contribute to the value of the matrix element (4) only when $V' = V$. Therefore the terms in $\overset{0}{\alpha}_{ii}$ will lead to Raman lines for which only the rotational energy changes. On the other hand, the terms in $\left(\frac{\partial \alpha_{ii}}{\partial \xi_\ell}\right)_0$, involving as they do the first power of ξ_ℓ , will contribute only to the matrix elements for which $V' = V \pm 1$, and which therefore are connected with a " fundamental " vibrational transition.

In both of these cases the dependence upon the rotational coordinates is identical. We can therefore treat the pure rotation band and the rotation vibration bands at the same time. Properties of the pure rotation band that are deduced from certain relations between $\alpha^{0}_{xx}, \alpha^{0}_{yy}, \alpha^{0}_{zz}$ will also hold for a vibration band, provided that for the particular vibration being considered the same relations hold between the quantities $\left(\frac{\partial\alpha}{\partial\xi_{l}}\right)_0$, etc. However, it must be remembered that this will not necessarily be the case. Placzek has discussed this point. We shall return to it later in connection with the spectrum of methane.

Only the integration over the rotational coordinates remains to be treated in (4). We shall not treat the general case further, but turn at once to the special case of the symmetrical top, referring to the recent paper of Placzek and Teller,$^{(11)}$ where polarization, selection, and sum rules are discussed without further specialization of the model. In the symmetrical top type of molecule $A = B \neq C$. Provided that this equality of two of the moments of inertia is due to symmetrical arrangement of the nuclei about the figure axis, rather than to a chance coincidence of the two quantities, we may safely assume that the plarizability shows the same symmetry, so that $\alpha_{xx} = \alpha_{yy} \neq \alpha_{zz}$. Since we are considering only the pure rotation spectrum, we need retain in the $\{\cdots\}$'s of (6) only the terms in α_{ii}^{o}, which are independent of the vibrational coordinates. Then (6) becomes

$$\alpha_{ZX} = \sin\psi \cos\theta \sin\theta (\alpha^{o}_{zz} - \alpha^{o}_{xx})$$
$$\alpha_{ZY} = \cos\psi \cos\theta \sin\theta (\alpha^{o}_{zz} - \alpha^{o}_{xx})$$
$$\alpha_{ZZ} = \sin^2\theta + \cos^2 \alpha^{o}_{zz} \qquad (7)$$
$$= \alpha^{o}_{xx} - \sin^2\theta (\alpha_{zz} - \alpha_{zz})$$

These expressions in (4) give the integrals which it will be necessary to evaluate. Since α^{o}_{ii} do not depend upon the coordinates, they may be taken out of the integrals, leaving only the circular functions.

The solution of the symmetrical top has been given by Reiche and Rademacher.(13)

The dependence of the resulting eigenfunctions upon the angles φ and ψ is given by

$$\psi(\theta,\varphi,\psi) = \Theta(\theta)\, e^{iK\varphi}\, e^{iM\psi} \qquad (8)$$

The function $\Theta(\theta)$ depends upon both the quantum numbers K and M. If these are replaced by

$$s = |K+M| \qquad d = |K-M| \qquad (9)$$

and the variable θ is changed to

$$t = \tfrac{1}{2}(1 - \cos\theta) \qquad (10)$$

the function Θ may be written

$$\Theta = t^{d/2}(1-t)^{s/2} \; F(t)$$

F (t) is a hypergeometric function which involved the quantum numbers s and d as well as an integer p. The energy W is then determined in terms of the moments of inertia a and C and the quantum numbers K and J, where $J = p + \frac{1}{2}(d+s)$,

(12)

$$W = \frac{h^2}{8\pi^2 A} \cdot J(J+1) + \frac{h^2}{8\pi^2}\left(\frac{1}{C} - \frac{1}{A}\right) K^2$$

If we let $B = \frac{h^2}{8\pi^2 cA}$; $\beta = \frac{A}{C} - 1$

the energy, measured in wave numbers, becomes

$$W = B\,J\,(J+1) + B\beta K^2 \qquad (13)$$

it is independent of M and of the sign of K. All three of the quantum numbers J, K, and M have physical meaning, being connected with the angular momentum of the system. J measures the total angular momentum, K its component along the figure axis of the molecule, and M its component along the specified direction in space. As is necessary for such an interpretation to hold, $|K| \leq J$, $|M| \leq J$.

From (8) and from the fact that φ does not appear in (7) it is clear that the integrals will vanish unless $K' = K$. (This shows at once that the frequencies of the pure rotation lines for the symmetrical top will not depend upon C, since C appears in the energy (10) only in the coefficient of K.) By the same reasoning $M' = M$ for the Z component of the scattered light. The other two components are most easily handled by conbining them to give

$$\alpha_{ZY} \pm i\alpha_{ZX} = e^{\pm i\varphi} \cos\theta \sin\theta \left(\alpha_{zz} - \alpha^{\circ}_{xx}\right) \qquad (14)$$

The selection rules for these two expressions (which give the intensity of right- and left-handed circularly polarized light) are $M' = M \pm 1$, respectively.

With the functions in their present form the selection rules for J are not immediately obvious. However matrix elements of Cos ϑ and sin ϑ alone, which determine infra-red intensities, are known to vanish unless $J' = J, J \pm 1$. Multiplying, by the usual matrix rule, it is found that the only matrix elements of sin ϑ cos ϑ that are different from zero are those for which $\Delta J = 0, \pm 1, \pm 2$.

The integrations over φ and ψ are performed immediately. that over ϑ (from $\vartheta = 0$ to $\vartheta = \pi$) has been replaced according to (9) by an integration over t from $t = 0$ to $t = 1$. It is found from (10) that

$$\begin{aligned} \sin^2 \vartheta &= 2\, t^{\frac{1}{2}} \, (1 - t)^{\frac{1}{2}} \\ \sin \vartheta \cos \vartheta &= 2 \, (1-2t) \, t^{\frac{1}{2}} \, (1 - t)^{\frac{1}{2}} \\ &= 2 \left[t^{\frac{1}{2}} \, (1 - t)^{3/2} - t^{3/2} \, (1 - t)^{\frac{1}{2}} \right] \end{aligned} \qquad (15)$$

In order that we may associate each element with the proper frequancy, our matrix elements are specified in terms of the same quantum numbers, J,K,M, by which the energy (12) is given. But before we can use wave functions in the form (11), J,K,M and ΔJ, ΔK, ΔM, must be correlated with values of s,d,p, and Δs, Δd, Δp. This is rendered somewhat complicated, in view of (9), by the necessity of considering whether K or M is the larger. For the case $M' = M + 1$, $M \geqslant |K|$, $J' = J + 2$, $K' = K$, one finds, from (9) and (12), $s' = s+1$, $d' = d + 1$, $p' = p+1$, so that a typical integral, say that for $t^{3/2} \, (1 - t)^{\frac{1}{2}}$ from (15) is

$$\int t^{d+2}(1-t)^{s+1} F_{s+1,\, d+1,\, p+1}(t)\, F_{s,d,p}(t)\, dt \qquad (16)$$

The function F, in the usual notation for the hypergeometric function, is given by

$$F_{s,d,p}(t) = F(-p,\ 1+s+d+p,\ 1+d;\ t) \qquad (17)$$

In the form used above the function is not yet normalized. For convenience we substitute

$$\Phi(s\ d\ p;\ t) = \binom{d+p}{p} F(-p,\ 1+s+d+p,\ 1+d;\ t) \qquad (18)$$

Now the normalization integral is$^{(13)}$

$$\int_0^1 t^d (1-t)^s\, \Phi^2(s\ d\ p;\ t)\, dt = \frac{(d+p)!\,(s+p)!}{(1+s+d+2p)\, p!\, (s+d+p)!} \qquad (19)$$

so that the normalized function is, instead of (11),

$$\theta(t) = \left\{\frac{(1+s+d+2p)\, p!\, (s+d+p)!}{(d+p)!\, (s+p)!}\right\}^{\frac{1}{2}} t^{d/2} (1-t)^{s/2}\, \Phi(s\ d\ p;t) \qquad (20)$$

Therefore (16), written with normalized functions becomes

$$\left\{\frac{(5+s+d+2p)\,(p+1)!\,(3+s+d+p)!}{(2+d+p)!\,(2+s+p)!}\ \frac{(1+s+d+2p)\, p!\, (s+d+p)!}{(d+p)!\,(s+p)!}\right\}^{\frac{1}{2}}$$

$$\cdot \int_0^1 t^{d+2} (1-t)^{s+1}\, \Phi(s+1,\ d+1,\ p+1;\ t)\, \Phi(s,d,p;t)\, dt \qquad (21)$$

By repeated applications of the two recursion relations$^{(13)}$

$$\Phi(d\ s\ p;\ t) = \frac{p+d}{1+s+d+2p}\ \Phi(d, s+1, p-1; t) + \frac{1+s+d+p}{1+s+d+2p}\ \Phi(d, s+1, p; t)$$

$$\Phi(d\ s\ p;\ t) = -\frac{p+s}{1+s+d+2p}(d+1, s, p-1;\ t)\ \frac{1+s+d+p}{1+s+d+2p}(d+1, s, p; t)$$

each function Φ in (21) can be expressed in terms of functions with various indices p, but all having the same s and d indices that appear as the exponents of t and (1-t). When these expressions for the two functions are multiplied together, only those products having common indices p need be retained, since the others vanish upon integration, due to the orthogonality.

The surviving integrals are given by (19). It remains only to collect the resulting terms into as compact a form as possible, and finally to replace s,d, and p in terms of J,K,and M. In the particular case chosen above in (16), only one term survives. The result is then

$$\frac{\left\{(J+k+1)(J+k+2)(J-k+1)(J-k+2)(J-M+1)(J+M+1)(J+M+2)(J+M+3)\right\}^{\frac{1}{2}}}{(2J+2)(2J+3)(2J+4)\left[(2J+1)(2J+5)\right]^{\frac{1}{2}}} \qquad (22$$

The same process for the first term of the expression (15) for $\sin\theta\ \cos\theta$ gives the same result with the opposite sign, so that subtraction of the two parts offers no difficulty. The intensity is proportional to the square of this matrix element.

Molecules with different quantum numbers M will all contribute to the same scattered line. We therefore sum the square of (22) over all values of M from -J to +J. This is accomplished, since M occurs only in the numerator, by means of the formulae

$$\sum_{0}^{n} x^{2} = \frac{1}{6}\, n\,(n+1)\,(2n+1)$$

$$\sum_{0}^{N} x^{4} = \frac{1}{30}\, n\,(n+1)\,(2n+1)\,(3n^{2}+3n-1)$$

We obtain, after simplification, and including the numerical factor,

$$\frac{2}{5}\;\frac{\left[(J+1)^{2} - K^{2}\right]\left[(J+2)^{2} - K^{2}\right]}{(2J+2)\,(2J+3)\,(2J+4)} \qquad (23)$$

We would now like to sum also over all initial values of K; but the populations of the~~se~~ states depends on K, since the energy contains K, so that the process is not simple. It is possible, however, to replace the summation over K by an integration. This involves only a slight error, except for light molecules for which relatively few rotational states are occupied — in which case the summation can be carried out explicitly. The integrals can then be reduced by integrations by parts to a form suitable for evaluation. Placzek and Teller (11) give expressions for this case, as well as diagrams of the intensity distribution over the rotation band for various values of .A/C. We shall be more interested in the case of light molecules.

The intensity of the components of the light scattered by a single molecule in the state J,K, averaging over all values of M, is proportional to the following for the indicated changes in J,

$$I_X\ (J,J+2) = \frac{3}{4}\ I_Z\ (J,J+2) = E_Z^2\,\gamma^2\ \frac{2}{15}\ \frac{\left[(J+1)^2-K^2\right]\left[(J+2)^2-K^2\right]}{(J+1)\ (J+2)\ (2J+1)(2J+3)}$$

$$I_X\ (J,J+1) = \frac{3}{4}\cdot I_Z\ (J,J+1) = E_Z^2\,\gamma^2\ \frac{4}{15}\ \frac{K^2\left[(J+1)^2-K^2\right]}{J\ (J+1)\ (J+2)(2J+1)}$$

$$I_X\ (J,J) = E_Z^2\,\gamma^2\cdot\ \frac{1}{15}\ \frac{\left[J\,(J+1)-3K^2\right]^2}{J\ (J+1)\ (2J-1)\ (2J+3)} \qquad (24)$$

$$I_Z\ (J,J) = E_Z^2\,\mu^2 + \frac{4}{3}\ I_X\ (J,J)$$

Here $\gamma = \alpha_{zz} - \alpha_{xx}$; $\mu = (1/3)\ (\alpha_{zz} + 2\ \alpha_{xx})$

We have omitted the factor $(\nu_o + \nu_{pq})^4$ contained in the intensity expression on p. 2-1 above, since it is effectively constant over any one rotation band.

The expressions (24) must still be multiplied by N_{JK}, the number of molecules in the state J,K, and the result summed over values of K from $-J$ to $+J$. Using equation (13) for $W_{J\,K}$ we obtain ~~$-B\,J\,(J\,1)$~~ ~~$-B\,K^2$~~

$$N_{J\,K} \propto (2J+1)\, g_{JK}\, e^{-\frac{BJ(J+1)}{kT}}\, e^{-\frac{B\beta K^2}{kT}} \qquad (25)$$

γ_{JK} is the quantum weight of the state J,K,. It contains the factor 2 when $K \neq 0$; in case the molecule contains identical nuclei the weight depends also upon the symmetry character of the wave functions - and especially the nuclear spin functions - for interchange of the identical nuclei. This dependence is discussed, for example, by Hund and by Dennison(14). For the NH_3 molecule γ_{JK} contains the factor 2 when K is divisible by 3 (including $K=0$). This makes very little difference in the intensity distribution in the band, due to the summation over K; it is necessary to include it, however, for low quantum numbers.

The experimental verification of this, as well as of the expressions (24) and (25) will be discussed in section 5.

Raman Effect Apparatus

The remainder of the present paper will be devoted primarily to the experiments that have been performed by the writer upon the Raman effect in gases. These may be divided into two parts. The first experiments were undertaken in an effort to resolve the rotational structure of a series of the simpler hydrocarbons, as well as carbon dioxide; these are described in section 6 below. The second part of the work involved photometric technique, by which the intensity distribution in the pure rotation band of ammonia was quantitatively determined. These results, as well as the frequencies in ammonia, are discussed in section 5. The present section will be concerned with the apparatus used for obtaining the scattered light, and with the method employed in the intensity determinations.

The apparatus used does not depart in principle from the usual design, but shows several modifications in construction. A metal cylinder 5" in diameter by 22" long and chromium plated on the inside serves as a reflector. Both the mercury arc and the quartz tube containing the gas to be studied extend the entire length of this cylinder. They are close together, at equal distances from the axis, so that each is approximately imaged by the reflector in the other. Scattered light emerges through a lens at one end of the gas tube into the spectrograph. At the other end of the tube is a black body, -- a metal tube somewhat wider than the quartz and about 10" long. The most completely black surface that was found was obtained by placing a plane piece of glass diagonally across the back of the black body tube, at an angle of about 12° with the axis. This was painted black on the back, and carefully cleaned on the front. For use in the ultraviolet there is of course no real need of the paint, unless too much visible light is scattered onto the plate from the inside of the spectrograph.

In the more recent work the black body has been replaced by a concave mirror placed at the back of the gas tube. By this means a certain amount of Raman light scattered by the gas in the opposite direction from the lens will be recovered by the mirror and put back into circulation. When the radius of curvature of the mirror equals the length of the tube, light from the quartz walls can not be reflected at the mirror in such a way as to reach the lens at the other end of the tube.

The increase in Raman intensity which should be gained in this way is limited to about 50% by the low reflecting power of metals in the ultra violet. Also there is no question but that the mirror makes a somewhat imperfect black background, due mainly to imperfections and dust on the surface. This may even counteract most of the gain in Raman light. Until pictures have been taken expressly to test this point, one can only say that the mirror has proved to be a satisfactory substitute for the usual cumbersome black body.

Light emerging from the other end of the quartz tube passes through a lens which throws an image of the black background upon the slit of the spectrograph. The effective diameter of the lens is controlled by the size of the quartz tube. The focal length is then so chosen that the optical system of the spectrograph is just filled. It is seen that the intensity of the Raman light entering the spectrograph does not depend on the diameter of the gas tube, but only on its length. The only advantage in a larger diameter is to obtain on the slit a larger image of the black background; when the dimensions are determined as outlined, the size of this image varies approximately with the square of the tube diameter. With the last form of apparatus used, the " black spot " was about .8 cm in diameter, with a quartz tube of about 1.8 cm. The use of a lens instead of a series of diaphragms to cut out illumination from the walls of the quartz tube has proved very satisfactory.

Several designs were attempted for the arc before a successful one was found. There were two principle problems. An arc may be started by the use of high potentials, blow torches, and choke coils. These methods, however, were not resorted to, the method of producing a mercury contact being relied on instead. The first means of accomplishing this was a reservoir 76.0 cm below the lower electrode of the arc, from which mercury could be forced by air pressure up through the arc till contact was made at the upper electrode. This was satisfactory in itself, except that the water jacket became somewhat complicated. However it brought up the second problem. If a mercury pool is used for the upper as well as the lower electrode, it dries up by evaporation in a few hours, and must be refilled, usually by the same process that is used in starting the arc. This proved especially inconvenient at night, when the arc developed an ability to get ahead of one,melt the glassware at the upper electrode and bring the exposure to a sudden conclusion.

The old-fashioned method of starting was finally resorted to, namely that of tipping the arc. To avoid the upper electrode trouble, both electrodes were placed at the same level, and connected by a very narrow U. The evacuating tube was led out of one of the legs, in such a way that it did not interfere with the water jacket, a single quartz tube , slipped on over the upper end of the U. Thus the water cooling becomes as simple and reliable as possible. The arc can be dismantled easily, which is necessary every one or two hundred hours of use to restore the ultra-violet transmission of the quartz. This is accomplished by passing a current of air through the tube, while it is heated in an oxygen flame. A further advantage of the design is the doubled effective length of the arc.

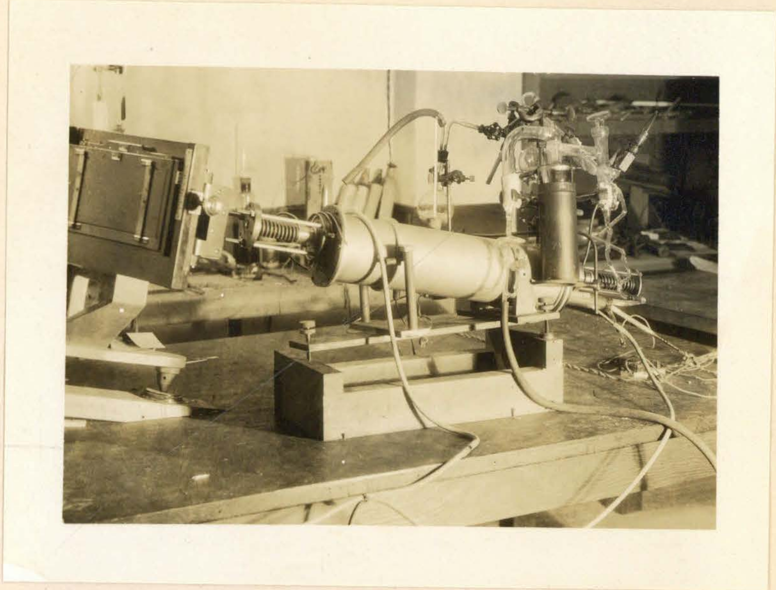
When the arc is started by tipping, it proves convenient (though not, I suppose, essential) to mount the whole evacuating system upon whatever tips. This was not difficult since a charcoal trap proved an entirely adequate substitute for the usual diffusion pumps. A flask and condenser were connected to the vacuum system, so that mercury could be distilled into the arc under vacuum. No other way was found for filling it after cleaning which did not introduce enough oxide to interfere with the starting process.

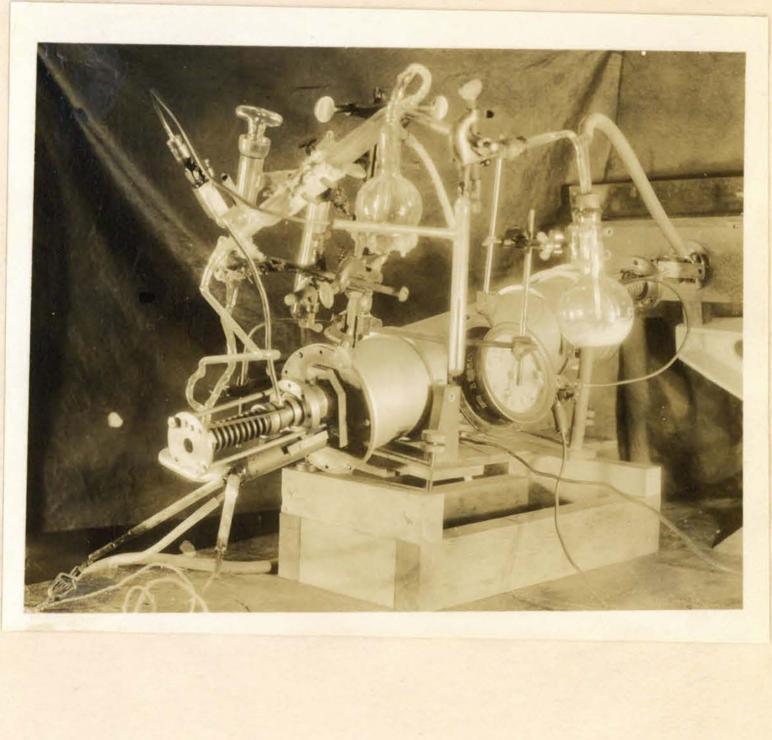
The first method of holding the gas tube was by means of sealing wax--inherited, I believe, from Rasetti. The most that can be said for this method is that it proved surprisingly effective; the quartz-to-steel joint withstood at times as high a pressure as 400 lbs. per square inch. There is no need of recounting the disadvantages. A great improvement was introduced by the use of gasket material, squeezed against the tube by the same scheme that is used in valve stem stuffing boxes. Instead of screwing one member into the other, as usual, it was pressed in directly, the force being exerted through a large spring. The force acting could be read on an experimentally calibrated scale, mounted beside the spring. Rubber gaskets are used at the back to facilitate access to the mirror. The lens is held between rubber gaskets, the same spring holding them tight that holds the packing. By this system no longitudinal strains are exerted on the quartz. Pressures higher than 120 lbs have not been used thus far, but the method has proved satisfactory within that range.

One of the principle advantages of this design is the ease with which the gas tube and lens may be taken down for cleaning. The construction is shown in fig.1, which is a horizontal section. The arc is therefore directly behind the gas tube and is not shown.

The general appearance of the apparatus is shown in Plate I. The electrodes of the arc, as well as the evacuating tube and water inlet are seen extending from the lower end of the reflector. In the lower picture one can see the arrangement for distilling mercury into the arc, and also the trap for condensing gases after drying in the flask at the right, in order to obtain them under pressure by evaporation.

PLATE I





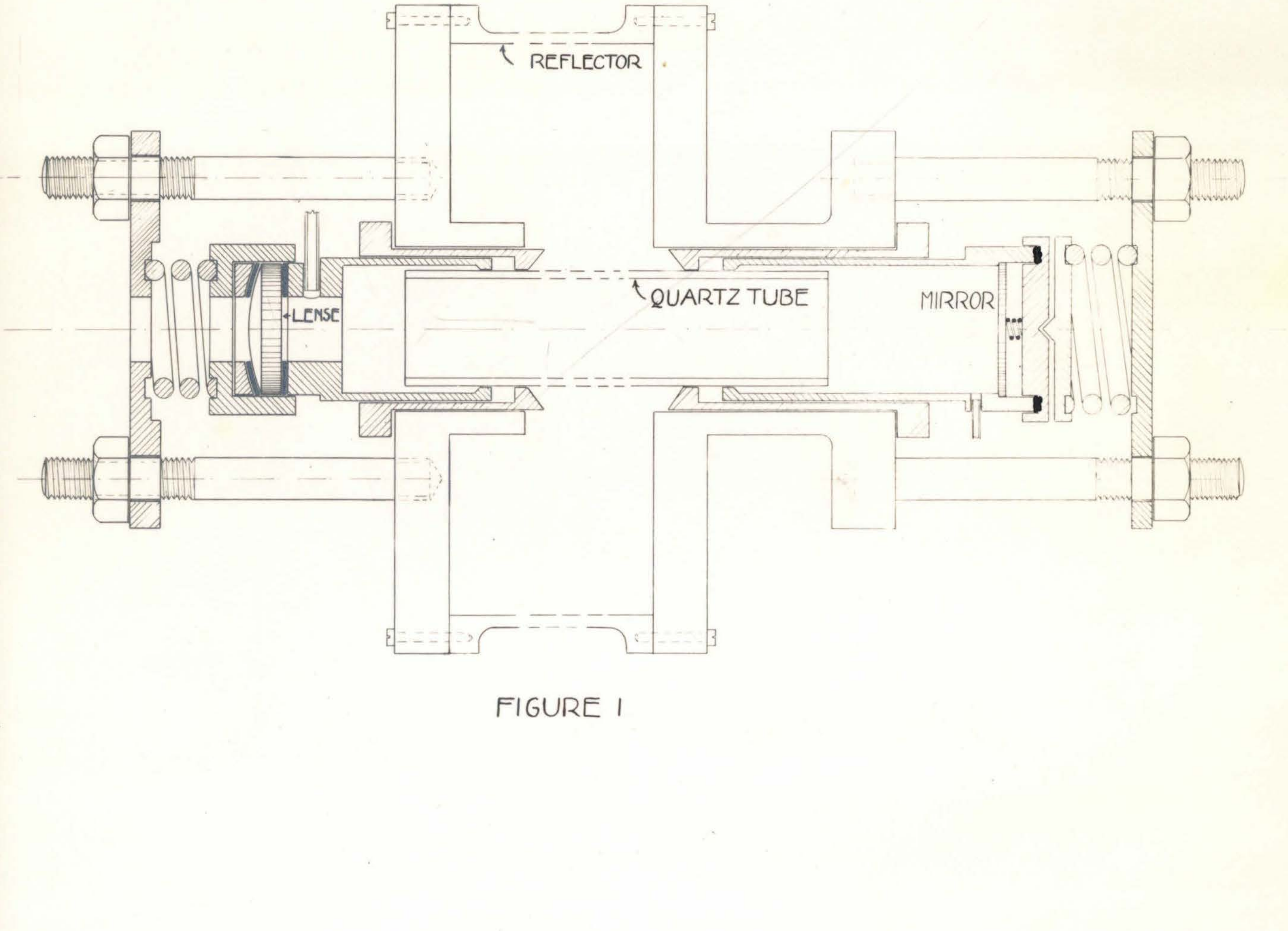
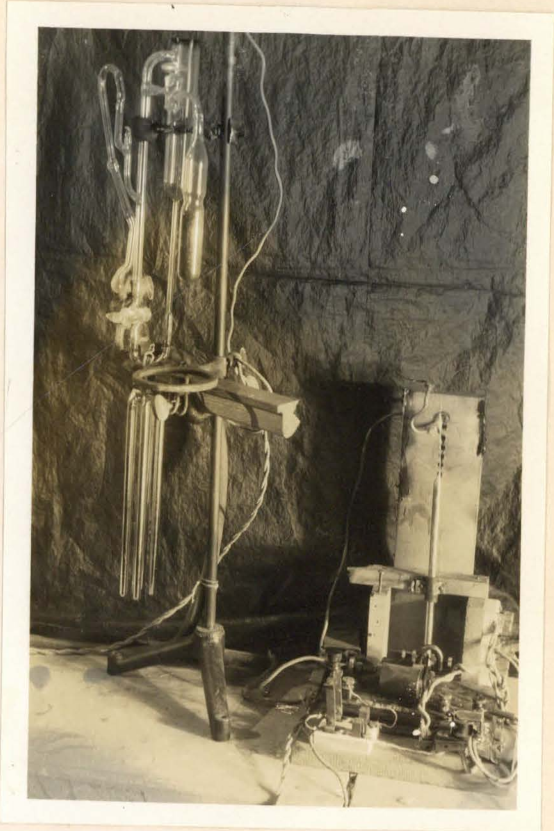


FIGURE 1



Thermostat

In order to get sharp spectra with the Hilger E-1 spectrograph it proved essential to keep the temperature of the room extremely constant. A variation of less than one degree during the three or four days would be evident in the picture. Accordingly a thermostat was designed --- after long hours wasted with simpler efforts--- which has proved very satisfactory. It is the usual mercury type, but evacuated in order to keep the surface in the capillary from becoming oxidized. The wire which makes contact with the mercury can be adjusted from outside by means of a small magnet which slides up and down with the wire; a spring balances most of its weight, and the slight friction of the wire against the capillary walls keeps it in place.

The thermostat was filled by distillation under vacuum; the tube through which the mercury entered was then closed by a stop cock, which must be actually in contact with the mercury. The thermostat is shown in Plate II.

The current controlled by the mercury contact actuated a telegraph relay, which in turn operated an automobile generator cut-out; this could handle the ten or fifteen amperes of alternating current which supplied the heater. The heating was done by means of wire coils strung in front of a large electric fan; this was mounted on the opposite side of the room from the thermostat, which was kept close to the spectrograph. A thermometer beside the thermostat would ordinarily show no more variation than a tenth of a degree. However, the lack of an icebox as well as an oven frequently caused grief. In the end the only answer to the mysterious vagaries of the ventilating system proved to be its elimination. With the air inlets entirely plugged up, the room became too hot only occasionly, instead of frequently.

Intensity Measurements .

For the determination of intensities each plate was calibrated by means of density marks obtained with light of very nearly the same wavelength as that of which the intensity was to be measured. Light from a small mercury arc placed at one side of the slit was reflected diffusely by a piece of white paper, placed about 18 inches in front of the slit, and large enough to fill the optical system of the spectrograph. This method insured that the slit was evenly illuminated over its length; it had the further advantage of giving a very low intensity. The exposure could then be of the same order of magnitude (at least photographically speaking) as the Raman exposure - being from one to four hours, while the Raman exposures varied from five to seventy hours. The various densities were obtained by means of a step weakener placed over the slit, the silvered side being turned away from the incident light so that any effect upon the quartz from prolonged exposure to ultra-violet light would be constant over the whole weakener.

The weakener was made by evaporating gold from a tungsten filament onto a window of fused quartz by the technique and with the assistance of Dr. John Strong of this institute. The steps were produced by uncovering a small amount of the surface at a time, a screen being moved along by a screw which could be turned from outside. This was accomplished by means of a small permanent magnet at right angles to the axis of the screw, which could be rotated by turning a strong horseshoe magnet held close to the glass of the bell-jar. Two advantages might be mentioned in gradually uncovering rather than covering the quartz surface. The screen can then be very close to the surface, insuring a sharp shadow, without fear of harming the metal coat that has already been applied. And since the rate of evaporation of the gold must be determined by trial, it is important that the steps of least density, which are the most important ones in the use of the weakener, be made last, instead of first. The width of the steps was one millimeter. This is close to the lower limit for use with grainy plates; it was chosen, however, in the hope of taking Raman pictures directly through the weakener. For this it is essential to have as large a number of steps as possible within the short region over which the slit is uniformly illuminated. Actually this method has not been tried, because the Raman light does not seem to be sufficiently uniform over even a small part of the slit.

The weakener was calibrated by comparison with another, kindly loaned by Dr. Hughes,* which had been calibrated directly by him with λ 2537, using a very sensitive thermocouple.

The density of the Raman spectra was measured with an excellent microphotometer, designed by Dr. Theodore Dunham, Jr., of the MT. Wilson Observatory, and built in their shop, for the use of which the writer is very much indebted to him. The density of the density marks was recorded by running over them with the same microphotometer, the setting being in every way the same. The microphotometer traces for three lines reproduced in Plate III show the general character of the data by means of which the plates were calibrated.

*National Reserach Fellow.

In some cases when the background of the Raman spectrum was high, this was gone over a second time with the microphotometer set to give larger deflections. The second record then gives more accurate readings for the individual lines, while the first gives the relation to the density marks. Such a procedure is possible only with a microphotometer which gives a deflection strictly proportional to the transmitted intensity. For example the Zeiss microphotometer departs widely from this relation.

The spectrum which is reproduced in Plate III is excellent for sharpness and intensity. The background of the spectrum, however, is no more dense than the general fog of the plate. This ordinarily very pleasing state of affairs is a disadvantage when it comes to the type of intensity measurements we are seeking. It means that the weakest lines are on the very lowest portion of the characteristic curve of the plate. This would not matter if it meant only discarding the weak lines, since others are strong enough to be accurately measured, even if they do not reach the straight section of the curve. But the broad overflow from the unshifted line produces a background, which, though it decreases rapidly, must be taken into account in measuring most of the Raman lines. In the region in which we are most interested this background is weak, but still important. Its intensity cannot be determined accurately any more than that of the weak Raman lines, because it falls on the tail of the characteristic curve. Hence the intensity of even the stronger Raman lines is rendered uncertain by the uncertainty of the local background.

The solution to this problem is clearly to raise the whole outfit up to a more sympathetic part of the characteristic curve. This could be done by partially exposing that part of the plate on which the spectrum is to be recorded either before or after the Raman picture is taken. If done in the most obvious way this would introduce errors, probably not large, but largely unknown. That is, the time of exposure as well as the color of the light would not be even similar for the background and for the lines, which we wish to measure relative to the background. This difficulty can be largely avoided by allowing light scattered inside the spectrograph to produce the background while the Raman exposure is being taken. This is easy to achieve, since the E-1 spectrograph has a shield over the central part of the lens to prevent just such an occurrence. This has only to be partially removed, the degree of removal depending upon the width of the slit and the time of the exposure contemplated. It is important, whether this or the more obvious method is followed, that the partial exposure should not include that part of the plate on which the density marks are to be made. Otherwise the characteristic curve will be raised up along with the spectrum, removing any advantage.

RAMAN EFFECT IN GASES

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Very intense ultraviolet light of wavelength 2536 Å from a mercury arc is caused to fall upon the gas molecules, which scatter the light in all directions. When this scattered light is analysed in a spectrograph, it is found that in addition to light of the original wavelength there is now also light of other wavelengths; this produces other lines on the photographic plate, which are known as Raman lines. The photographs below show how the position and intensity of the Raman lines vary when the light is scattered by different kinds of gases.

The change of wavelength of the light during the process of being scattered is always associated with a change in energy of the scattering molecule; the energy change of the molecule is proportional to the frequency shift of the light. In the pictures below are shown only shifts due to changes in rotational energy of the molecule.

The change in frequency, measured in wave number units, is given by the expression

$$\Delta \nu = \frac{h}{8\pi^2 cI}\Delta J(2J + \Delta J + 1)$$

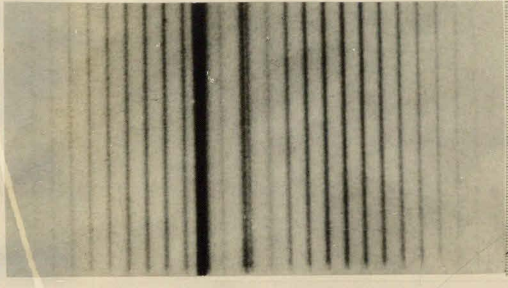
where J is the rotational quantum number of the initial state
ΔJ is the change in J during scattering
I is the moment of inertia of the molecule.

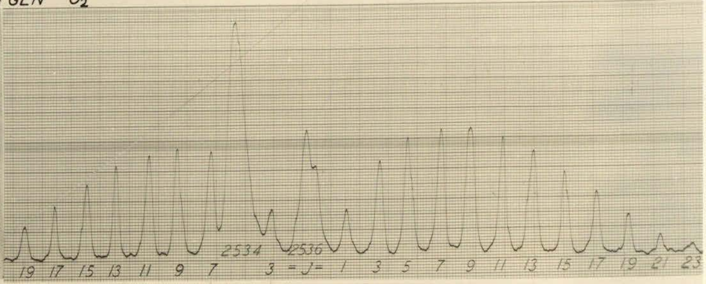
Since I occurs in the denominator, the frequency shift $\Delta\nu$ will be less for larger molecules, and this is seen to be true in the cases shown below.

The line marked "Hg 2534" in all the pictures has nothing to do with the question in hand. It is simply a frequency of the incident light which cannot be seperated out, and so tags along and obscures a small part of the Raman band.

The intensity of the exciting line, Hg 2536, is intrinsically very many times greater than that of 2534, so that the Raman lines due to it appear as shown, while those due to 2534 (which would form an exactly similar pattern) are so very weak that they make no impression whatever on the photographic plate. However, the strength of the two mercury lines appears approximately equal in these pictures because the intense line 2536 is very strongly absorbed by mercury vapor in the spectrograph, while 2534 is not absorbed. Were this method not resorted to, the exciting line would be so much overexposed as to hide a large part of the Raman band.

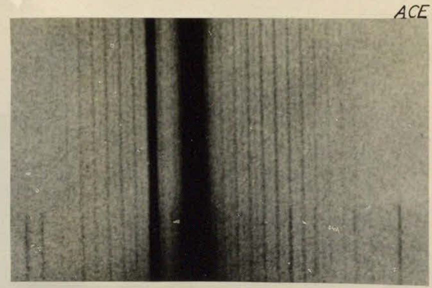
OXYGEN O_2

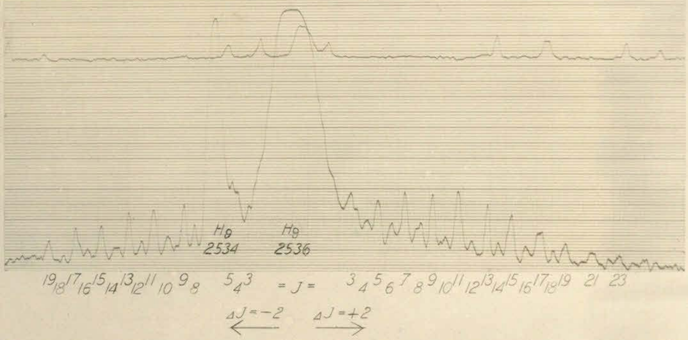




When the molecule is linear, as in the first three cases, ΔJ is always either plus or minus two. The Raman pattern is then rather simple. The light which produces each line is scattered by molecules which are initially in a particular rotational state. The gradual variation in intensity as we go from one Raman line to the next is due primarily to the different numbers of molecules in the various initial rotational states. Under each line is given the quantum number J of the initial state of the molecules which produced that line. Lines to the right (low frequency) side of the exciting line are the result of an increase in J, those to the left result from a decrease in J.

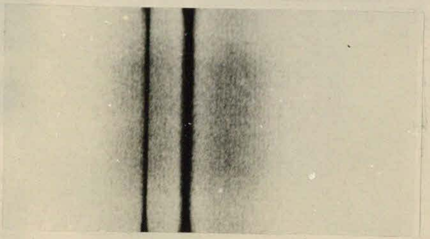
ACETYLENE HC-CH

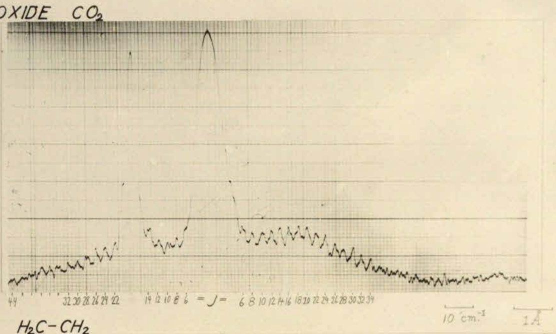




Since all of these molecules have a plane of symmetry, all initial values of J may not occur. In fact it is seen that in oxygen J is always odd, in carbon dioxide J is always even, while in acetylene, due to the nuclear spin of the hydrogen atoms, both even and odd values of J occur, but the latter three times as frequently as the former. This leads to the "alternating intensities" seen in the case of acetylene.

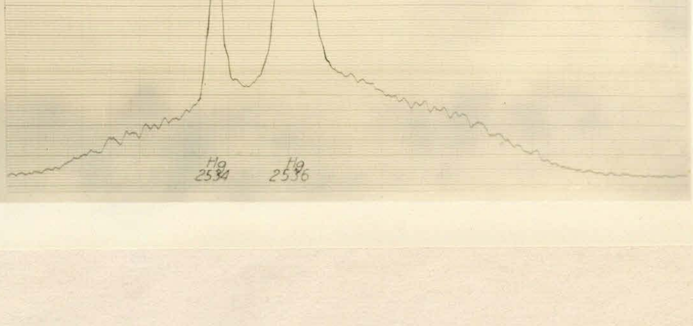
CARBON DIOXIDE CO_2





When, as in ethylene, the molecule is not linear, we may have $\Delta J = \pm 1$ as well as ± 2. The frequency shifts of the lines due to $\Delta J = \pm 1$ are only about half as great as the others, and the lines bunch together close to the exciting line, obscuring the pattern in that region, and changing the envelope of the microphotometer curve.

ETHYLENE H_2C-CH_2



Intensities in the Pure Rotation Band of Ammonia.

For the experiemental test of the theoretical intensities derived in Section 3, the ammonia molecule is an ideal subject. It belongs to the symmetrical top class. The moment of inertia, $A = 2.80 \cdot 10^{-40}$ gm cm^2, is a perfect compromise. It is small enough so that the lines may be resolved easily, but not so small as to restrict unreasonably the number of rotation lines available.

Values of J as high as 10 or 12 will be sufficiently populated at room temperature to produce lines. For higher states approximations would be needed in calculating the intensities, but up to 12 the summation over K can be carried out explicitly without undue labor. The pressure that can be used in the apparatus is limited, it is true, to about 100 pounds, but this proves sufficient. The fluorescence, which Rasetti and others have reported as making the vibration lines difficult to measure, was not found to give trouble, probably because of the high dispersion used.

A further-- and not inconsiderable-- advantage in the use of ammonia for this purpose is the fact that other interest attaches to the results. The intensity measurements will be shown to provide a means of setting limits upon the moment of inertia C. No great accuracy is to be expected in this direction, since the intensity is relatively insensitive to changes in the ratio of the two moments. But it is possible to show in this way that the nitrogen nucleus is not far from the plane of the hydrogens, thus confirming this now well-established result. The doubling of the infra-red bands has been explained by Dennison(15) on the basis of a very low pyramid. The two positions of equilibrium of the nitrogen ----one on each side of the plane---are then separated by so low a potential barrier that the frequency with which the molecule turns inside out is nearly $1 cm^{-1}$ when in the ground vibrational level. Both Dennison and Uhlenbeck(16) and Rosen and Morse(17) have discussed quantum mechanically the vibration of the nitrogen along a line perpendicular to the plane of the hydrogens; they find that the observed vibrational frequencies are compatible with assumed potential energy functions only if the height of the pyramid is closely specified. The figures obtained in the two papers for this distance are remarkably close, namely .38 and .365 Å . There appears to be little possibility of questioning the essential correctness of these results, but the very novelty of the means by which they have been obtained makes it of some interest to confirm them from an entirely independent argument.

With this in mind, intensities have been calculated from the expressions given in section 3 for the pure rotation

Raman lines on the low frequency side of the unshifted line (Stokes lines) for three different values of $\beta = A/C-1$: the plane model, $\beta = -5$; the model indicated by the analysis of Rosen and Morse, $\beta = -.367$; and the spherically symetrical model for which $\beta = 0$. In all these cases it has been assumed that $A = 2.80 \cdot 10^{-40}$ gm cm^2 and $T = 42^\circ$C. The constants in the exponentials of (25), section 3, are then $B/kT = .0449$, and $B\beta/kT = -.0164$, $-.0224$, and 0, in the three cases mentioned above. With these values, the product of (24) by (25) was summed explicitly over all values of K from $-J$ to $+J$. The results are collected in Table 1.

Since it is not feasible to measure the absolute intensity of Raman lines, only the relative intensities of the various lines in each case are of interest. Therefore the calculated intensities are expressed in such units for each model that the line $J = 4 \rightarrow J = 6$ will have the same intensity in all cases. This line--- rather than, say, the most intense line of the spectrum--- is chosen as the point of contact, because the calculations for the different models then agree better for a larger number of lines. The comparison with experiment was therefore simplified by this choice.

The experimental intensities given in Table 1 were obtained as described in section 4. The ammonia was taken from a commercial cylinder, dried over sodium hydroxide flakes,

Table I

Intensity Distribution in Pure Rotation Band of Ammonia.

Stokes Lines						
Calculated Intensities $A=2.80\ 10^{-40}$; $T=42^{\circ}C$				Observed Intensities	Initial J	
Sphere	Plane	Morse no spin	Morse		$\Delta J=2$	$\Delta J=1$
2.15	1.72	2.49	1.86	†		1
4.33	3.64	5.94	3.88	6.80	0	2
8.63	7.90	7.31	8.26	8.14		3
12.90	12.11	12.02	12.29	11.04	1	4
7.30	7.76	8.55	7.75	7.93		5
13.30	14.08	13.82	13.81	13.22	2	6
4.35	6.48	5.88	5.91	6.41		7
12.00	12.40	12.61	12.32	12.55	3	8
1.49	3.48	2.78	2.99	4.34		9
10.73	10.73	10.73	10.73	10.73	4	10
.25*			.75*	1.28		
9.14	8.28	8.92	8.70	8.50	5	
7.11	6.75	6.91	7.01	7.48	6	
4.81	4.91	4.96	4.96	5.55	7	
2.95	3.22	3.21	3.16	4.66	8	
1.60	1.94	1.87	1.85	2.12	9	
.79	1.10	.98	.89	1.07	10	

Anti Stokes Lines			
Morse	Observed	$\Delta J=-2$	$\Delta J=-1$
1.55			2
3.88	2.83	2	3
5.77	5.38		4
7.85	6.41	3	5
4.52	4.50		6
7.39	6.99	4	7
2.90	3.40		8
5.48	5.76	5	9
1.22			10
4.00	4.14	6	11
.20			12
2.60	3.37	7	
1.80	2.28	8	
1.07	1.65	9	
.57		10 ~~11~~	

†Observed, but too weak to measure

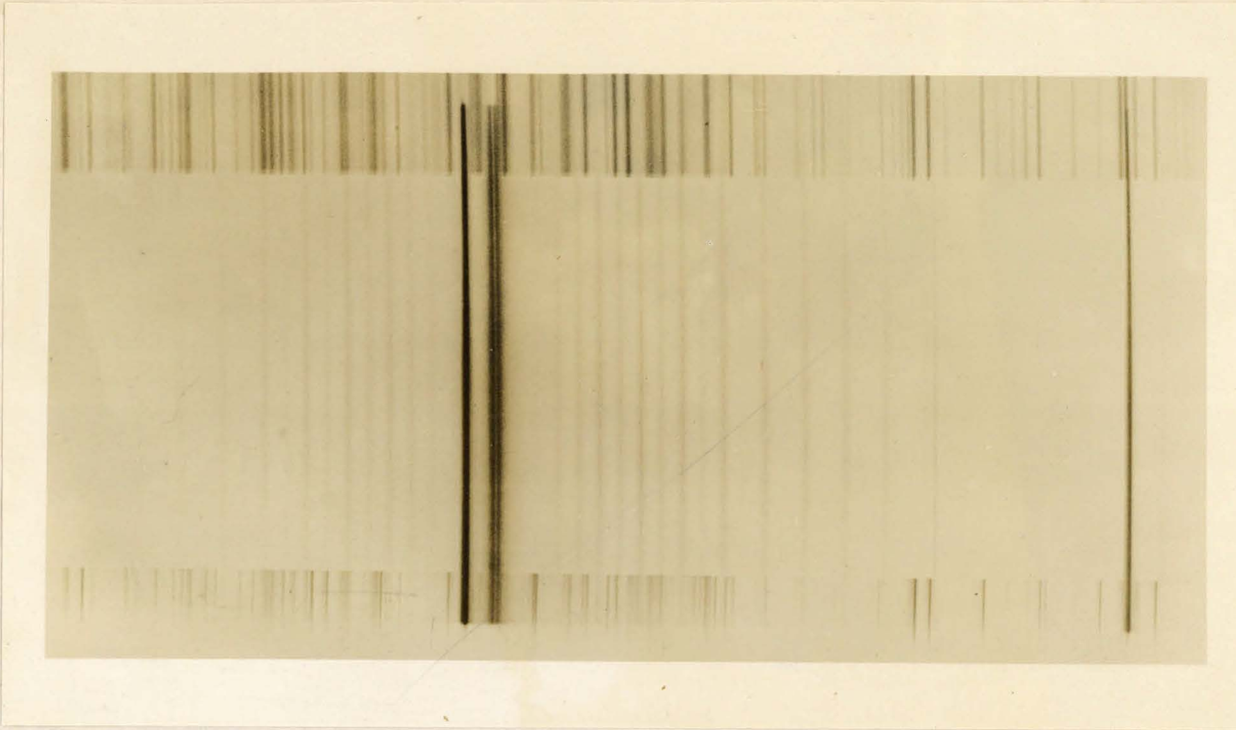
*Obtained graphically

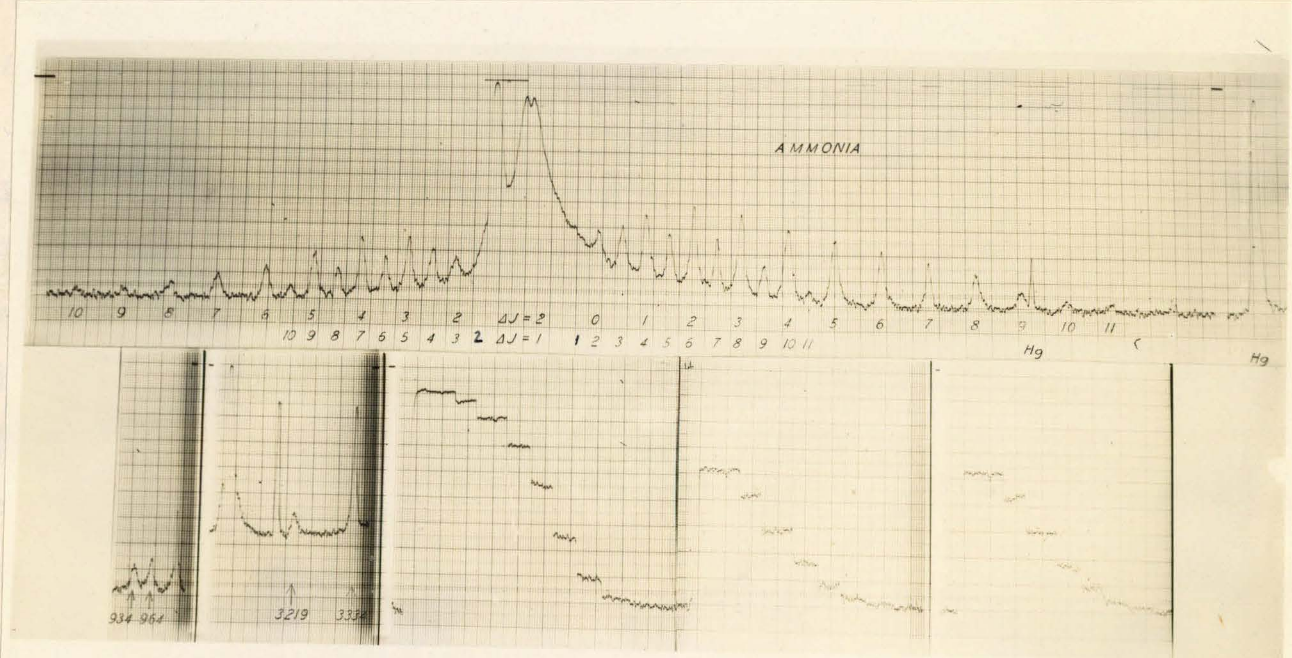
condensed, and evaporated into the apparatus. Pressures of 75 to 100 pounds per square inch were employed. In most cases a moderately wide slit was used. Since the intrinsic width of the rotation lines -- at least at the pressures mentioned -- is one or two frequency units, this serves to increase the intensity without broadening the lines appreciably.

A typical spectrum is reproduced in Plate III. The greater sharpness of the Hg lines is clearly evident. The very effective absorption of Hg 2537 by mercury vapor in the spectrograph is also evident. This detail of technique was introduced by Rasetti and has become what may be called standard practice. It is especially effective in connection with the Hilger E-1 spectrograph, since the total light path is then more than ten feet. The advantage obtained in this way is sufficient to justify the complications and added expense of working in the ultraviolet; the greatly increased intensity in this region may therefore be considered as a free gift.

To facilitate the comparison of experimental and theoretical intensities, these are plotted for the various lines, both Stokes and anti-Stokes, in Plate IV. The length of the solid lines represents the intensities calculated for the " Morse " model ($\beta = A/C - 1 = -.36{\times}6$; height of the pyramid $= .367 \cdot 10^{-8}$ cm.). The other symbols are explained in the Plate. Initial values of J for the various branches are given below each line.

PLATE III

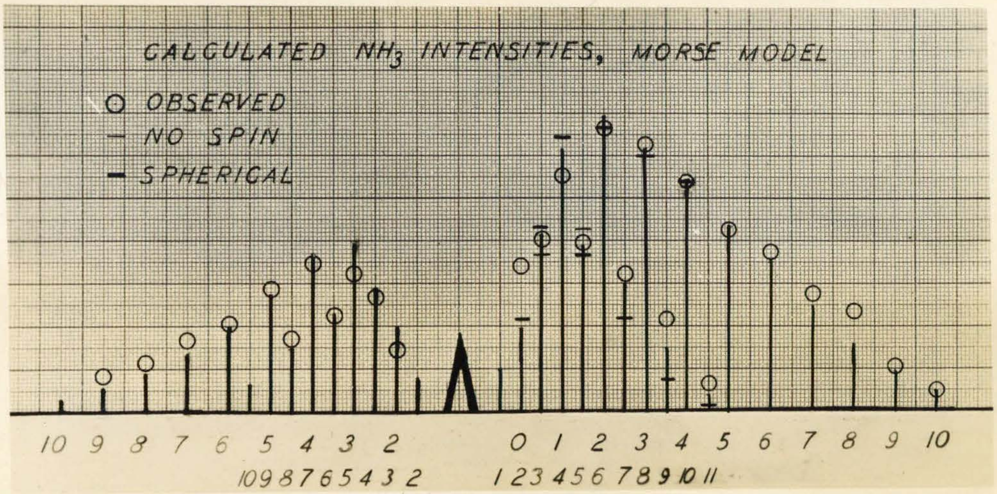



AMMONIA
10 9 8 7 6 5 4 3 2 ΔJ = 2 0 1 2 3 4 5 6 7 8 9 10 11
10 9 8 7 6 5 4 3 2 ΔJ = 1 1 2 3 4 5 6 7 8 9 10 11
Hg
Hg
934
964
3219
3334

In regard to the effect of the symmetry properties and nuclear spin, it is clear from Table 1 that it approaches zero for high values of J. For the S branch it is not more than a few percent even for J=1, and 3; for J=0, the correction is about one third. Turning to the R branch, we find greater sensitivity to the spin effect; the lines for J=3 and J=5 are altered by 13% and 9.4% respectively, and in opposite directions, so that they change places in order of intensity. In plate IV the intensities calculated for no spin are plotted only for these two lines, since the deviations in the other cases are too small to detect experimentally. It is clear, however, when these two are compared with the experimental points, that the spin effect must be taken into account to give agreement.

We may now examine the general agreement between experiment and the calculations from the Morse model. Out of the 27 lines plotted all but 5 show as close agreement as one could expect. These are the transitions of J from 0 → 2, 1 → 3, 8 → 10 in the S branch; 9 → 10 in the R branch; and 3 → 1 in the O branch. The first of these, 0 → 2, is too close to 2537 for accurate measurements. It is believed that 8 → 10 falls upon a weak Hg line, though this has still to be confirmed directly. The error in 1 → 3 is only about 11%, and is not distressing. This leaves only one anti Stokes line, 3 → 1, with an error of 17%, and one Stokes line in the R branch, 9 → 10, which show definitely unsatisfactory agreement. The general trend of the

PLATE IV


CALCULATED NH_3 INTENSITIES, MORSE MODEL
○ OBSERVED
– NO SPIN
▬ SPHERICAL
10 9 8 7 6 5 4 3 2
0 1 2 3 4 5 6 7 8 9 10
10 9 8 7 6 5 4 3 2
1 2 3 4 5 6 7 8 9 10 11

intensity distribution follows the calculated values very well.

In particular it is seen that the ratio of intensity of Stokes to anti-Stokes lines is just as predicted. The fear expressed by Amaddi and Placzek(18) that the anti-Stokes lines were stronger than predicted may therefore be laid aside. It was based only upon rough intensity estimates.

The accuracy of the observations is not sufficient to distinguish between the Morse and the plane model for NH_3, and values for the latter (see Table 1) are not included in plate IV. Calculated intensities for the spherical model are, however, included for those Stokes lines in which the deviation is appreciable. In no case does this model give better agreement than that for $\beta = -.366$ (with the possible exception of the line $0 \rightarrow 2$, which we have discarded as being too close to 2537). On the other hand $3 \rightarrow 4$ and $5 \rightarrow 6$ show slight preference for the Morse model, while $7 \rightarrow 8$ and $11 \rightarrow 12$ are conclusive evidence that the molecule is nearly planar.

Raman Frequencies in Ammonia.

Frequencies for both the rotation and vibration Raman lines in ammonia have been determined by completely independent measurements of the two best plates. In obtaining the shift in frequency, the average of the Stokes and anti-

Stokes rotation lines is taken as the frequency of the exciting line. In Table 2 are given the observed Raman frequencies, which are averages of the Stokes and anti-Stokes lines on the two plates.

Lines for $\Delta J = \pm 2$ (S and O branches) are listed separately from those for $\Delta J = \pm 1$ (R and P branches). This is because the frequencies are fitted more closely if in the two cases different constants are taken for the dependence of the moment of inertia upon the rotational energy. Calculated frequencies have been obtained by the use of the following expression for the rotational energy levels.

$$E/hc = B_0 J\,(J+1) + B_0 \beta K^2 - B_0' J^2\,(J+1)^2 \qquad (1)$$

The second term is not important, since K does not change. The frequencies of the S branch lines are found to be

$$B_0\,(4J+6) - B_0'\,(8J^3 + 36J^2 + 60J + 36) \qquad (2)$$

and of the R branch lines

$$B_0\,(2J+2) - B_0'\,(J+1)^2\,(4J+4) \qquad (3)$$

These quantities are given in Table 2, with $B_0 = 9.92$, $B_0' = .00052$ for the S branch and $B_0 = 9.92$, $B_0' = .00023$ for the R branch. This use of different values for B_0' is a purely empirical procedure, and appears to have little justification beyond the agreement produced. In any case it proves impossible to fit the observed lines by means of

Table II.

Frequency of Ammonia Rotation Lines.

	J	1st order frequency $2J+2$	$(B=9.92)$	Correction $8J^3+\cdots$	$(B'=.00023)$	Calculated frequency	Observed frequency	Differ.
Anti-Stokes	1	4	39.68	32	.007	39.67	39.67	+.00
	3	8	79.36	256	.059	79.30	79.48	-.18
	5	12	119.04	864	.199	118.84	119.25	-.41
	7	16	158.72	2048	.471	158.25	158.38	+.13
	9	20	198.40	4000	.920	197.48	197.38	+.10
	11	24	238.08	7112	1.640	236.44	236.50	-.06
	J	$4J+6$	$B_0=9.92$	$4J^3+\cdots$	$B'=.00052$	Net Calc ν	Obs.	
Stokes	0	6	59.50	36.	.016	59.48	59.8	-.3
	1	10	99.20	140.	.073	99.13	99.17	-.04
	2	14	138.88	364.	.187	138.69	138.62	+.07
	3	18	178.56	666.	.346	178.21	178.25	-.04
	4	22	218.24	1364	.71	217.53	217.50	+.03
	5	26	257.92	2236.	1.16	256.76	256.92	-.16
	6	30	297.60	3420.	1.78	295.82	295.82	+.00
	7	34	337.28	5034.	2.62	234.66	334.50	+.16
	8	38	376.96	6916.	3.59	373.37	372.5	-.43
	9	42	416.64	9243.	4.80	411.84	411.9	-.06
	10	46	456.32	12236.	6.36	449.96	449.9	+.06

expressions (2) and (3) and a single set of constants. It may be that a different form for the last term of (1) would be more satisfactory. The theory behind this question will need further investigation.

Clearly the S branch gives the greater accuracy and we shall consider it alone. It yields a value of $2.790 \cdot 10^{-40}$ for the moment of inertia A. This is an excellent average of previous determinations. The constants 9.92 and .00052 are remarkably close to those given by Dickinson, Dillon, and Rasetti,(19) who found 9.921 and .00063, using the energy formula

$$E/hc = B_0 \, (J + \tfrac{1}{2})^2 - B_0 \, (J + \tfrac{1}{2})^4$$

They were not troubled by the R branch, since they did not observe it. Amaldi and Placzek (18) give frequencies which are systematically about 1.5 cm^{-1} higher than ours. They are more interested in other features of the spectrum and do not discuss these values.

Turning to the vibration lines, we find the following frequencies from the two plates measured, and from the results of other authors.

Intens.	Plate 38A	Plate 47A	Mean	Amaldi and Placzek	Dickinson Dillon & Rasetti
3	934.6	933.7	934.2	933.8	
			30.1	30.5	
4	964.5	964.1	964.3	964.3	
2	3219.2	3219.1	3219.1		
10	3334.2	3334.0	3334.1	3334.2	3333.6

The values for the doublet at 950 cm and the symmetrical vibration frequency at 3334.1 are in sufficiently good agreement with Amaldi and Placzek to require no further discussion of their significance. In the former case the lines are quite broad, and greater accuracy than 5 cm^{-1} has little meaning. This is evident from the lower microphotometer curve in Plate III, when one remembers that the two lines are 30 cm^{-1} apart.

Placzek has predicted that the fourth fundamental frequency of NH_3, which ~~never~~ had not yet been observed, should appear faintly in the Raman effect. It is believed that the line observed at 3219.1 is the fundamental of this vibration.

Rotational Raman Effect in Methane, Ethane, Ethylene Acetylene and Carbon Dioxide.

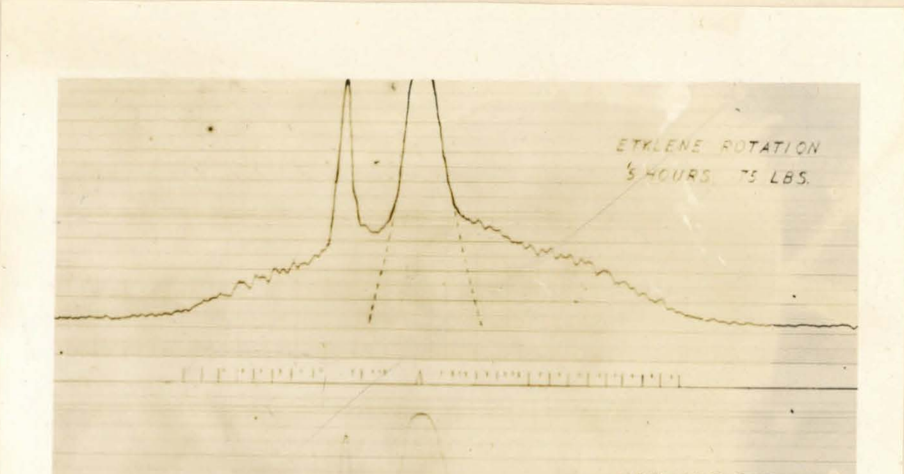
Methane.

A series of the simpler hydrocarbons was investigated with the primary purpose of obtaining resolved rotation; relatively few polyamotic molecules had at that time been studied with sufficient resolving power for that purpose.

Methane had been studied by Dickinson, Dillon and Rasetti, who observed a vibration-rotation band from which the moment of inertia in the normal state was found to be 5.17. They found lines corresponding to $\Delta J = \pm 2$ but not ± 1; they found no pure rotation lines. The latter result is confirmed by Bhagavantam and others. In studying methane again, it was hoped to obtain the P and R branches of the vibration band, and to establish more definitely the status of the pure rotation lines.

Some evidence was found of P and R branches, but, due to the very low intensity, it was not entirely conclusive. The region in which these lines should fall was complicated by the vibration lines of ethane and propane, which must have been present to the extent of 5 to 10 percent as impurities. The R and S branches were observed, and agree well with the results of Rasetti. The vibration-rotation spectfum is shown in the lower microphotometer curve reproduced in Plate V. The very intense Raman line shown is at 3916 cm^{-1} and is due to the symmetrical vibration; it has no rotation wings. The rotation lines marked in the margin go with the Q branch at 3022, which is due to a degenerate vibration; the average polarizability is changed very little by the vibrational motion, but α_{xx} and α_{zz} are changed in different directions, destroying the spherical symmetry of the polarizability tensor. It is for this reason that rotation lines appear, though the Q branch is much weaker than that of the completely symmetrical vibration.

It was found, in agreement with the qualitative results of Rasetti and of Bhagavantum that the pure rotation band of methane was certainly of a lower order of intensity than that of molecules without spherical symmetry. This is in accord with the theory. Some slight evidence was found, after exposures of 100 hours, of very faint lines at about the position that rotation lines would be expected to appear. It is thought, however, though it has not been definitely established, that these are extremely weak mercury lines. Plate V shows the striking contrast between the pure rotation of methane and of ethylene. The faint lines referred to are marked, and one may judge for himself of their reality. No critical test is to be found in the frequencies corresponding to them because of the interaction of rotation and vibration, discussed by Teller and Tisza(8).


ETKLENE ROTATION
15 HOURS 75 LBS.
METHANE ROTATION
97 HOURS 90 LBS.
METHANE VIBRATION
90 HOURS 160 LBS.
Hg 2753
Hg 2760

Ethylene

The structure of the pure rotation of ethylene shows a curious grouping of the lines into pairs. This is more evident in the lines further from the exciting frequency, as one would expect, for here there is not the complication of transtitions in which $\Delta J = \pm 1$, which may be expected to obscure the patterns in the closer part of the band.

On the other hand for the lines with largest frequency shift observed, the pairs appear to be drawing together somewhat.

The plate grain makes measurement of this fine structure very uncertain. This can be very considerably remedied by studying enlargements made from the original in the following way. While the enlargement is being made, the original plate is moved steadily in a direction parallel to the Raman lines. The image in the enlargement is then blurred in this direction, but is still in sharp focus in the direction perpendicular to the lines. The results of this process are shown in plate VI where are reproduced enlargements made in this way of the rotation bands of ethylene, carbon dioxide and ethane. The first two of these may be compared with the enlargements made in the usual way and reproduced somewhat imperfectly in the " Exhibit " following section 4. It is important not to move the plate further than is necessary to wipe out the grain. Otherwise a blemish on the plate is transformed into a line which it may be difficult to distinguish from the genuine ones. In Plate VI one can see how small a distance the plate was moved; for example the very short lines, which are iron standards, do not extend appreciably further than in the original.

In spite of the pairing of the lines, which is so clearly evident to the eye, the frequencies as measured on the comparator are found to be very nearly equally spaced. In Table 3 are given the values obtained from the enlargement reproduced, as well as from three different plates measured directly. In both cases the values given are averages of Stokes and Anti-Stokes lines. The agreement is on the whole surprisingly close.

Values are calculated for $B_0 = .920$, and are seen to fit moderately well, if we assume that only lines for which $\Delta J = \pm 2$ are observed. This value corresponds to a moment of inertia of $30.1 \cdot 10^{-40}$ gm cm^2. Since ethylene is not precisely a symmetrical rotator, this is to be interpreted as a mean of the two nearly equal moments of inertia A and B. This interpretation has been confirmed by a calculation of the energy levels from the formulae given by Dennison(14,II) for the asymmetrical top. It was found that for values of J up to six the departure from the symmetrical top formula was negligeable, when the mean of A and B was used for the moment of inertia.

The value 30.1 for $\frac{(A+B)}{2}$ ~~As~~ may be compared with $A = 32.52$ and $B = 30.32$, calculated from Pauling's values of the interatomic distances, and assuming the tetrahedral angle of $109^\circ 28'$.

Table 3.

Ethylene Rotation

Observed frequency from enlargements	Observed frequency from 3 plates	Mean	Calculated frequency B_0=.920	Diff.	J
10.5		10.5	9.20	- 1.30	1
12.8		12.8	12.88	+ .08	2
16.0		16.0	16.56	+ .56	3
19.7		19.7	20.24	+ .54	4
23.2		23.2	23.92	+ .72	5
25.8		(25.8)			
27.3	27.35	27.32	27.60	+ .28	6
30.4 31.7	31.45	31.5	31.28	- .22	7
35.1	35.1	35.1	34.96	- .14	8
38.7	38.85	38.78	38.64	- .14	9
42.6	42.5	42.55	42.32	- .23	10
45.9	45.9	45.9	46.00	+ .10	11
49.8	49.5	49.65	49.68	+ .03	12
53.5	53.1	53.3	53.36	+ .06	13
56.9	56.9	56.9	57.04	+ .14	14
59.7	60.1	59.9	60.72	+ .82	15
63.6 65.0	64.1	64.1	64.40	+ .30	16
66.1					
68.9		68.9	68.08	- .82	17
72.5		72.5	71.76	- .74	18
74.9		74.9			
76.2		76.2	75.44	- .76	19
79.3		79.3	79.12	- .18	20

The disagreement here is small. It may be due to a faulty interpretation of the band. When the pairing of the lines is recognized, it proves possible to arrange them in two sets, both having linear spacing, but with slightly different constants. Details of such an assignment need not be entered into, since no explanation has been obtained for it, and the data is insufficient to make it definitely superior to the assignment given above. It is mentioned to show that a small error in B_0 may be made from such a source. It may well be that the rotational oscillations about the double bond will need to be taken into account.

The further question of the absence of lines with $\Delta J = \pm 1$ is not serious, since they would appear only in that part of the spectrum which is pretty well clogged up already. The agreement obtained in Table 3 is sufficient to assure that the general aspects of the assignment of the observed lines are correct.

Ethane

A great many pictures have been taken of ethane, because its spectrum shows just sufficient indications of structure to keep one's optimism flourishing. There is clear evidence in several pictures of structure in the vibration-rotation band.

However not enough lines are present to make possible a definite interpretation. Apparently the observed lines are due to systematic variations in the intensity of the actual fine structure, which cannot itself be resolved. The spacing is not too small to permit resolution of the individual lines; but each line is probably broad, due in part to perturbation of each molecule by its neighbors. This could be reduced (as has been noted especially in CO_2, (20) and by Bhagavantum(21) in O_2, and other gases) by using lower pressure, but then the intensity is not sufficient.

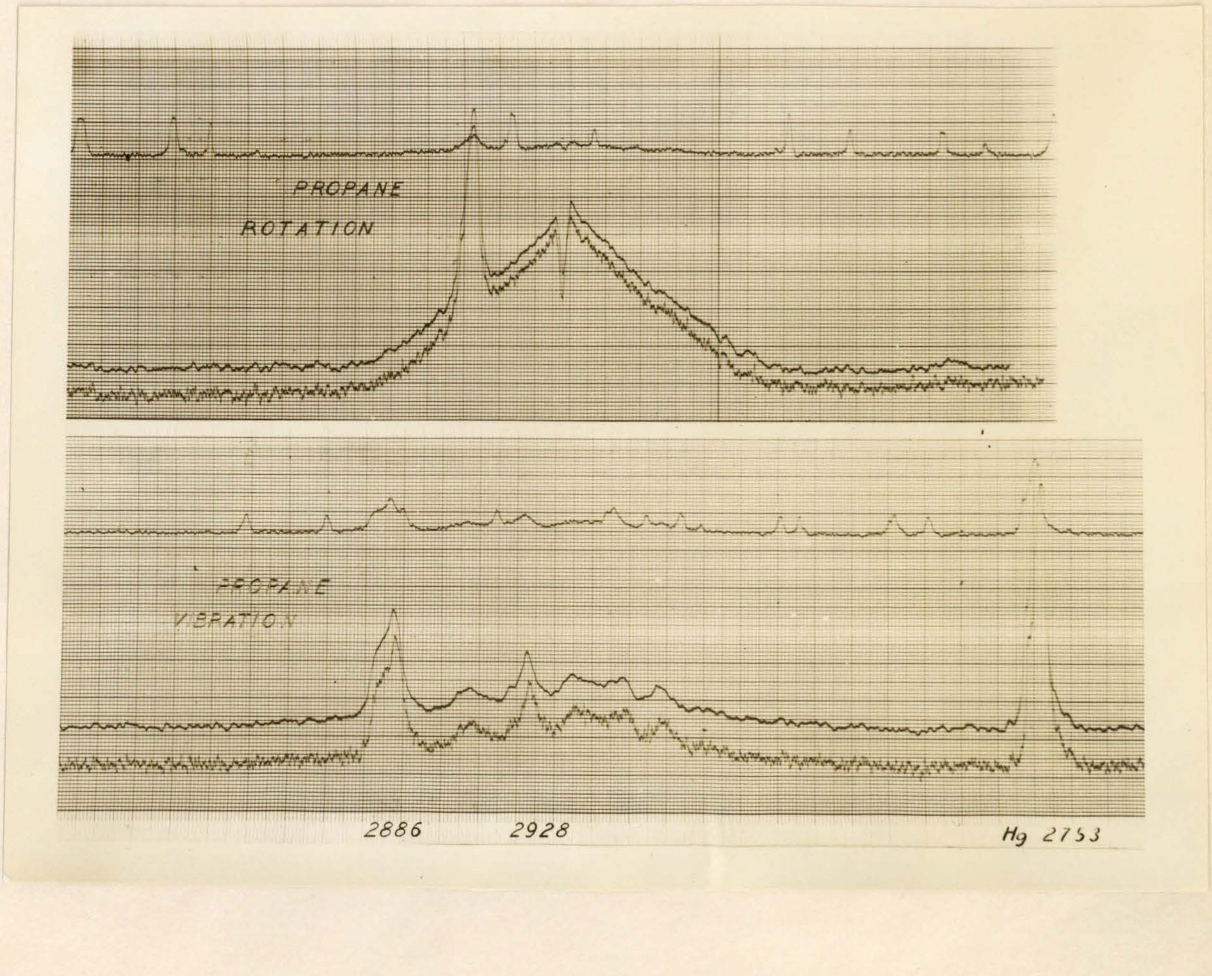
The pure rotation band has shown resolution only in the last picture taken. A series of rather broad lines are clearly evident, and yield the frequencies given below. These are averages of readings taken directly from the plate, and from enlargements such as the one reproduced in Plate VI. The spacing is seen to be close to 7.2 cm^{-1}.

Observed Rotation Structure in Ethane

Stokes	Anti-Stokes
37.8 cm^{-1}	36.3 cm^{-1}
45.0	44.0
52.4	52.2
59.6	59.7
66.2	66.5
73.1	73.6
80.5	79.9
86.0	87.1
91.9	

PLATE VII

Ethane Vibration.



We obtain the right order of magnitude for the moment of inertia C if we assume that this broad structure is due to changes of two in K with constant J. But K is permitted to change only if the two polarizability components α_{xx} and α_{yy} perpendicular to the molecular axis are different, and there seems no reason for expecting this here.

In addition to these intensity maxima there is a much finer structure. This has a spacing of a little more than a quarter of the other, namely 1.9cm^{-1} . If it were exactly one quarter, we would suppose that every fourth line of the fine structure was weaker (or stronger) than the rest, giving the banded effect we have pointed out. The accuracy of measurement so far is sufficient to throw doubt on this explanation without making it definitely untenable.

Such considerations become relatively unimportant when one notices that the spacing of the narrow structure is almost identically half of that observed in ethylene. The appearance also of ethylene vibration lines upon the ethane plate confirms the presence as an impurety. See, for example, Plate VII. The gas was used directly from a small pressure tank supplied by Matheson Company. It may be possible that the impurity is due in part to photochemical decomposition. Efforts will be made to remedy the difficulty if it is due to other causes.

In the meantime we may suggest a further explanation of the observed spectrum. One would expect, if both ethane and ethylene are present, that beats would occur between the two sets of rotation lines. This may well be the cause of the broad regions of greater intensity mentioned above. It is to be noted that we must here assume ethylene lines for which $\Delta J = \pm 1$, although no such lines were observed in the spectrum of ethylene itself. This is the weakest point in the suggested interpretation of the ethane plate. Let us pass over it, and assume also that ethane lines are present for both $\Delta J = \pm 1$, and ± 2. Then, if broad regions of greater intensity are due to " beats" between the ethane and ethylene rotation lines, a simple calculation leads to the value 1.45 cm^{-1} between the ethane lines, which in turn corresponds to a moment of inertia for ethane of $38.2 \cdot 10^{-40}$ gm cm^2 . This compares favorably with 38.6 , obtained from Pauling's inter-atomic distances, This interpretation is intended more as an interesting suggestion than as an evaluation of the moment of inertia. The agreement, however is encouraging. It is hoped that better resolution may yet be attained.

Carbon Dioxide

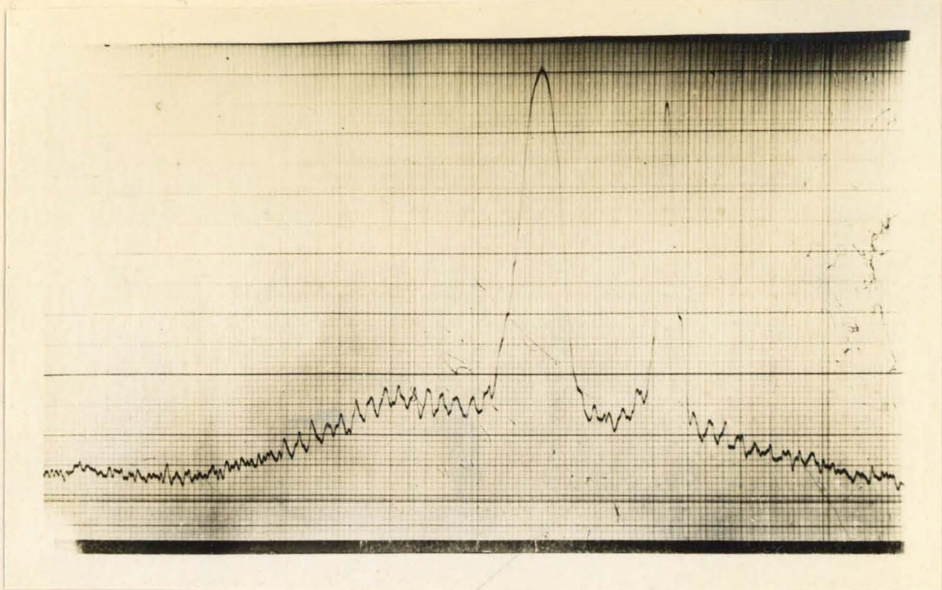
Entirely satisfactory resolution has been obtained of the rotation band of carbon dioxide. This remains, so far as I am aware, the largest molecule which has yet been subjected to such analysis. A large part of the work involved in obtaining this sprectrum, as well as in its interpretation was performed by Prof. Houston. The results have been published in the Proceedings of the National Academy, 17, 229,' 31, from which extracts are included below. The resulting value for the moment of inertia is $70.2\cdot10^{-40}$ gm cm^2. Plate VI shows an enlargement made by the process described above, of the rotation band of CO_2.

Acetylene

The moment of inertia of acetylene is so small that no difficulty is encountered in resolving its structure. The spectrum and a microphotometer curve are shown in the " Exhibit " above. Measurement of the lines yielded a value for A of $23.45\cdot 10^{-40}$ gm cm^2, which agrees very well with the infra-red result of Hedfeld and Mecke(22), 23.509. The alternating intensities shown in the reproduction are fully explained by symmetry considerations when a nuclear spin of 1/2 is assigned to each hydrogen atom(14).

Photon Spin

A few words may be said about an attempt which has been made to re-examine the experimental foundations of the



ROTATIONAL RAMAN SPECTRUM OF CO_2

The measured values of the wave-length changes are given in table 1. Since the position of the over-exposed exciting line is rather hard to determine, the shifts are measured from a point half-way between the positively and negatively shifted lines. This differed by 0.36 cm.$^{-1}$ from the estimated position of the mercury line.

TABLE 1

			SHIFT IN CM.$^{-1}$	
n	*J*	OBS.	CALC.	OBS.
1	0	...	2.36	.....
2	2	...	5.51	.....
3	4	...	8.66	− 8.93
4	6	11.58	11.81	−11.67
5	8	14.76	14.96	−14.91
6	10	18.25	18.11	−18.02
7	12	21.59	21.26	−21.46
8	14	24.52	24.41	−24.67
9*	16	27.58	27.56	.....
10	18	30.66	30.71	−30.73
11	20	33.92	33.86	−33.29
12	22	37.08	37.01	−36.97
13	24	40.21	40.16	−40.23
14	26	43.42	43.31	−43.36
15	28	46.45	46.46	−46.52
16	30	49.84	49.61	−49.50
17	32	52.46	52.76	−53.46
18	34	55.54	55.91	.....

The calculated wave numbers are from the equation

$$\nu = (3.150/8)(4J + 6). \qquad (1)$$

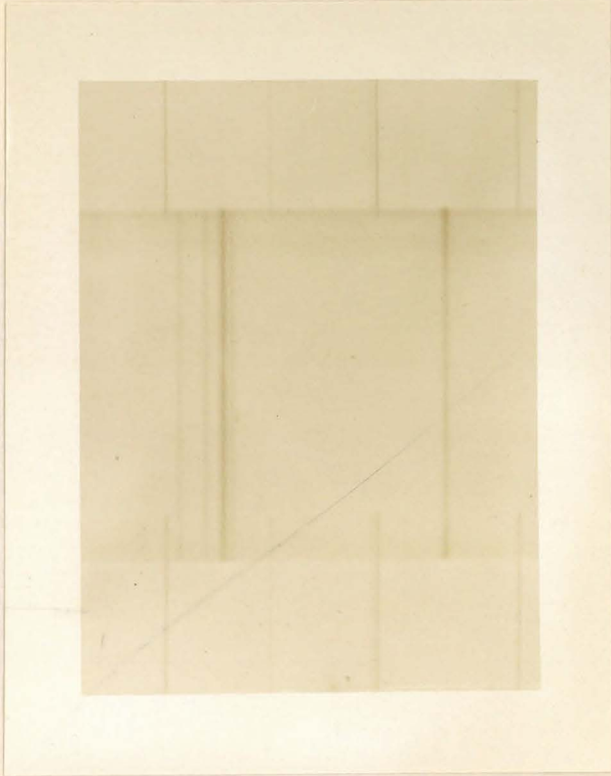
This formula, together with the values used for *J*, shows that the rotational quantum number, *J*, changes by two units in a transition, that only even rotational states are present, and that the moment of inertia is 70.2×10^{-40} g. cm.^{2} Since the positions of the lines are probably not more than 0.5 cm.$^{-1}$ in error, this value for the moment of inertia is probably correct within one or two per cent.

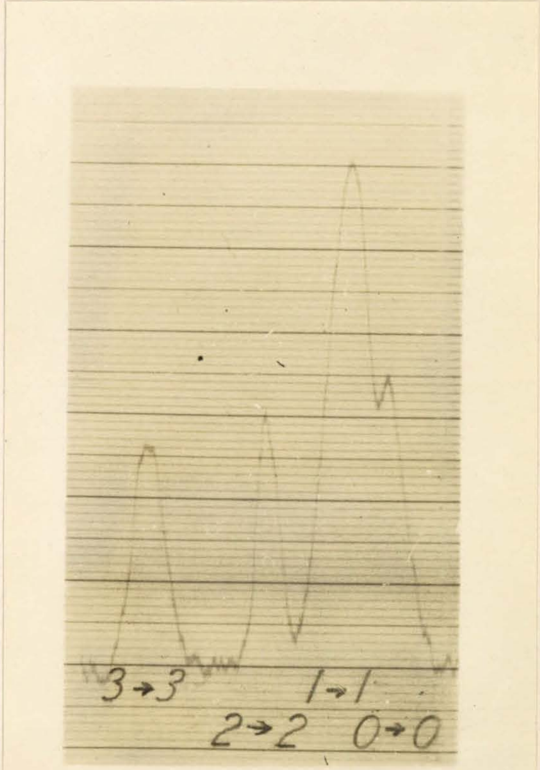
" photon spin " theory which Raman has recently advanced. Studying the intensity of the perpendicular and horizontal components of light scattered by hydrogen, Bhagavantam(23) has secured evidence that the results of Manneback's theory do not hold. A large part---approximately half--- of the discrepancy has been found to be due to an error of calculation in Manneback's paper(10) which has since been pointed out also by Placzek and Teller.(11)

It appears to the writer very probable that the remaining discrepancy is to be attributed to experimental errors, principally in the polarization technique, rather than in the photometry itself as Placzek(11) and others have suggested.

It was noticed that the aspects of the theory attacked by Raman and Bhagavantam could be checked without using polarization, provided the intensities of the four lines observed in the Q branch of the vibration band could be compared with sufficient accuracy. The method rests upon the fact that the intensity of the Q-branch lines is due in part to a term depending upon the rotation of the molecule, and in part to a term independent of this. The ratio of the two terms is approximately the same for three of the lines, and therefore cannot be determined from their intensities. But for the line 0 → 0 the " rotational term " drops out. The ratio of the two terms for the other lines may therefore be obtained by

PLATE VIII





H_2
Vibration
Q-Branch

comparing the intensity of the 0 → 0 line with the others. The exact bearing of this ratio upon the spin theory is somewhat involved and need not be gone into here. Since the " rotational term " is much smaller than the other one, considerable accuracy is needed to make the experiment conclusive. From 5 to 10% should suffice.

The Q-branch of hydrogen as obtained with the Hilger E-1 spectrograph is shown, with a microphotometer curve, in Plate VIII. It is seen at once that the line 0 → 0 is too close to 1 → 1 to be measured with certainty. Many plates were made without obtaining resolution better than that shown. The results were in favor of the usual as against the spin theory, but could not be called conclusive. Since in this case only a conclusive answer is of interest, the method had to be given up.

In conclusion, the writer wishes to acknowledge his indebtedness to Prof. William V. Houston, under whose direction, and, in large measure, by whose hand the foregoing experiments have been carried out. His interest in the work was a constant pleasure and inspiration.

Summary of Results.

An account is given of the relation of the theory of the Raman effect developed by Placzek to the theory based upon the Kramers Heisenberg formula. The equivalence of the two is shown in the general case.

An outline is given of the procedure used by Prof. W.V.Houston and the writer in evaluating the integrals resulting from this theory for the intensities of the individual rotrotation lines for molecules of the symmetrical top class.

The results of this calculation are verified experimentally in the case of ammonia gas, using accurate photometric technique. It is shown (1) that the general intensity distributtion over the pure rotation band is as predicted; (2) that the effect of the nuclear spin of the hydrogen atoms must be taken into account; (3) that the relative intensity of the R-branch and S-branch lines corresponds to a molecule which is nearly planar, in agreement with results from the infra-red spectra. The frequencies of the rotation and vibration lines of ammonia are also discussed. The line at 3219 cm^{-1} is interpreted as due to the unsymmetrical vibration of the hydrogen nuclei, not previously observed.

The rotation structure of a series of the simpler hydrocarbons has been investigated. Methane shows no pure rotation, in agreement with theory. The rotation band of acetylene has

been obtained, and gives $A = 23.45 \cdot 10^{-40}$ gm cm^2. Ethylene shows a structure with slight irregularities which have not been fully accounted for; the moment of inertia is found to be approximately $30.1 \cdot 10^{-40}$ gm cm^2. An interpretation is suggested for the results with ethane which yields $A = 38.2.10^{-40}$ gm cm^2. The resolution in the case of carbon dioxide is entirely unambiguous and gives $A = 70.2 \cdot 10^{-40}$ gm cm^2.