ON THE VIBRATIONAL SELECTION PRINCIPLES IN THE RAMAN EFFECT

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Various writers[1,2,3] have noted that the displacements of energy levels involved in the Raman effect should be those obtainable by superposition of two "allowed" spectral transitions. In other words, $\nu(ac)$ is a possible Raman shift if we can write $\nu(ac) = \nu(ab) + \nu(bc)$, where $\nu(ab)$, $\nu(bc)$ are possible emission or absorption frequencies. The reason for this is that the theoretical expression for a Raman line of frequency, $\nu_0 + \nu(ac)$, excited by incident light of frequency ν_0 is proportional to

$$(\nu_0 + \nu(ac))^4 \left\{ \left| X^{(R)}_{(ac)} \right|^2 + \left| Y^{(R)}_{(ac)} \right|^2 + \left| Z^{(R)}_{(ac)} \right|^2 \right\}, \qquad (1)$$

where

$$P^{(R)}_{(ac)} = \frac{E}{2h} \sum_b \left[\frac{P(ab)Z(bc)}{\nu_0 + \nu(bc)} - \frac{Z(ab)P(bc)}{\nu_0 + \nu(ab)} \right] e^{2\pi i [\nu_0 + \nu(ac)]t}. \qquad (2)$$

Eqs. (1, 2) are the same as those recently given by Hill and Kemble,[3] and embody the results of the Kramers dispersion theory. Here $X(ab)..$ denote the matrix elements of the Cartesian components of the electrical moment of the molecule in the unperturbed state, while $X^{(R)}(ab)....$ denote the perturbed or "Raman" values of these elements under excitation by plane polarized incident radiation having its electric vector $E \cos 2\pi\nu_0 t$ along the z direction. Eq. (2) involves the amplitudes connected with transitions to what we shall term the "intermediate" states b rather than the amplitudes $P(ac)$ of direct transition from a to c, thus substantiating the remarks made at the beginning of the paragraph.

Notation, etc.—Before even stating the particular problem connected with Eqs. (1, 2) which we aim to discuss, it is perhaps well to introduce some nomenclature and qualifying remarks. We shall suppose except in the final paragraphs that the molecule is diatomic, and shall ignore the rotational fine structure. The letters v and n will denote, respectively, the vibrational quantum number and the totality of electronic quantum numbers. To separate the vibrational and electronic effects, it is often convenient to use a double index n, v for the matrix arguments instead of a single index such as a, b, c in Eq. (2). The term "level" is to be understood to comprise all the vibrational states having a given set of electronic quantum numbers, and we shall use the term "state" for the individual vibrational members of a level. The normal level will be denoted by n_0. Two levels a, b will be said to "combine" if the unperturbed amplitude $P(ab)$ does not vanish; i.e., if $\nu(ab)$ is a possible absorption (or emission)

frequency, but not necessarily a possible Raman shift. We shall use the term "changes" in discussing the alterations of quantum numbers in ordinary absorption or emission transitions, and shall reserve the word "displacements" for the total alterations in quantum numbers between the initial and final Raman states. It is to be clearly understood that the term "intermediate" relates merely to the position of a state such as b in the products in Eq. (2), and does not at all imply that its energy is intermediate between those of the initial and final Raman states, as this is usually not the case.

Problem of the Small Raman Displacements in the Vibrational Quantum Number.—The most commonly studied Raman lines represent displacements in the vibrational, but not in the electronic quantum numbers. However, the important intermediate states involved therein probably belong to *excited* electronic levels, as the absolute intensities of pure vibration spectra are low and hence the amplitudes connected with transitions to intermediate vibrational states belonging to the normal level are small.[4] Thus Raman displacements corresponding to infra-red vibrational frequencies are due in a certain sense to excitation of electronic absorption lines usually in the ultra-violet. The incident light is ordinarily in the visible region, and so could not excite these lines with close resonance, but nevertheless does react somewhat with the amplitudes of ultra-violet absorption, affording an illustration of what has sometimes been termed "weak quantization," especially in the old quantum theory. Now when there are electron jumps, the selection principles for the vibrational quantum number are quite different from what they are in pure vibration spectra. Whereas we can only have $\Delta v = \pm 1$ in simple harmonic, pure vibration motions, there can be enormous changes in v if there are simultaneous changes in n. In the latter event cases are known in which v changes by 20 units or so.[5] Now if a Raman displacement is expressible as the result of two consecutive jumps, one might at first thought expect Raman displacements of say 20 + 20 or 40 in the vibrational quantum number (taking this rather extreme example for concreteness).

More precisely, the allowed changes in v are determined by the requirement that the initial and final states are to have the same inter-nuclear distances during appreciable time fractions of their respective motions. This is the rule advanced semi-empirically by Franck[6] and justified quantum-mechanically by Condon. Now the nuclei move slowest and spend relatively the greatest time at the extremes r_{min}, r_{max} of their vibrational paths for a given state. Hence two states combine intensely if they have a common extremum of the inter-nuclear distance r. This extremum can, however, be a maximum for one state and a minimum for the other. In particular, if we start with a given vibrational state v of a given electronic level n, changes are particularly favored to two vibrational states of another electronic level n' (viz. the pair $r'_{min} = r_{min}$ $r'_{max} = r_{max}$ if $r_{min} < r'_0 < r_{max}$; the pair $r'_{max} = r_{min}$, $r'_{max} = r_{max}$ if $r'_0 < r_{min}$ the pair $r'_{min} = r_{min}$, $r'_{min} = _{max}$, if $r'_0 > r_{max}$; here r'_0 denotes the equilibrium value of r in the

state n'). This, as Condon shows, is in good agreement with experiment. If one plots initial and final vibrational quantum numbers as abscissa and ordinates, the intense changes form a "Condon" parabola, and the ordinate or abscissa representing a given state intersects this parabola twice, giving the two favored transitions from this state. To apply these ideas to the Raman effect let us start in Eq. (2) with a given initial level $a = n_0$, v_0 belonging to the normal electronic level. Let us further consider the effect of all the intermediate vibrational states belonging to a given electronic level n. In view of the foregoing there will be two of these states, say n, v_1 and n, v_2 which combine particularly with n_0, v_0. If the Raman displacement is purely vibrational, the final state c belongs to the normal level n_0. But the intermediate state n, v_1 can combine with another vibrational state, say n_0, v_3, of the normal level besides n_0, v_0, as there are two favored transitions. Similarly n_0, v_2 can combine with another state n_0, v_4 besides n_0, v_0. As a Raman displacement is compounded from two ordinary changes, one might expect intense Raman lines corresponding to displacements $v_0 - v_3$ and $v_0 - v_4$ in the vibrational quantum number, besides of course the Rayleigh scattering $\Delta v = 0$. Such displacements represent passage from one side to the other of the Condon parabola for the intermediate level. When finally one includes all the different intermediate electronic levels in (2) one would obtain an enormous range of possible displacements in v, of large amounts if the important intermediate levels have widely different moments of inertia from the level n_0.

These hasty conclusions are not in agreement with experiment. Actually the intense Raman lines, at least in gases, involve shifts in frequency equal to the fundamental line of a pure vibration spectrum, or perhaps in some cases the first harmonic. This means that the common Raman displacements in the vibrational quantum number are only one unit, or possibly sometimes two units. The flaw in the foregoing argument predicting large displacements is the following. One must remember that according to the Condon-Franck principle, a given state combines, though with greatly varying intensity, with all the vibrational states belonging to another electronic level. In particular, we assumed in the preceding fine print that a given state combined practically entirely with only a pair of states of another level, instead of with all other vibrational states of this other level, though with reduced intensity. The reduction in intensity is, as a matter of fact, not large for states which are immediate neighbors of either of the states (the favored pair) that combine most strongly with the given initial state; this is especially true if the vibrational quantum numbers are large. In forming the sum in (2), one must therefore include the contribution of every vibrational state belonging to a given intermediate level. Furthermore, in adding these contributions, one must be very careful to consider the *phases* of the matrix elements involved therein. One finds that the phase effects give reinforcement when the initial and final levels a and c are the same, the case of Rayleigh scattering. (At least this is true for the z component, as $z(ab)z(ba) = |z(ab)|^2 > 0$ and so all the terms to be added have the same sign, as with a given intermediate level the variation in the denominator from term to term in the summation in (2) is negligible.) On the other hand, because of the di-

versity of phase factors for the different intermediate states belonging to a given electronic level, one suspects that the various terms in the summation will largely annul each other if the initial and final states a and c differ widely in their value of v. If, however, the states a and c are adjacent, i.e., if the Raman displacement in v is only one unit, the annulment might be very incomplete, as this case is very close to that of reinforcement. By a somewhat similar qualitative reasoning, Hill and Kemble[3] briefly stated that the phase relations explain why there are only small Raman displacements in the vibrational quantum number. The purpose of the present paper is to give a more quantitative and rigorous proof of this proposition of the usual absence of all displacements except the fundamental $\Delta v = \pm 1$. The writer is informed that C. Manneback is also publishing a proof, but by a method somewhat different from ours, so that the present note is perhaps not superfluous.[7]

Mathematical Preliminaries.—We shall first develop a multiplication scheme for what we shall call "hybrid matrix elements," whose use is the essence of the proof. Let Ψ_v and Φ_v ($v = 0, 1, \ldots$) be two *different* sets of orthogonal normalized functions of a variable r, so that

$$\int \Psi_v^* \Psi_{v'}\, dr = \delta_{v'}^v, \qquad \int \Phi_v^* \Phi_{v'}\, dr = \delta_{v'}^v, \tag{3}$$

with the asterisk denoting the complex conjugate. For example, and more especially for our purposes, Ψ_v and Φ_v might be the vibrational wave functions for two different electronic levels. Let $f(r)$ be any function of r, and also if desired of the operator $\partial/\partial r$. Expand $f(r)\Psi_v$ as a series in the Φ_v, thus

$$f(r)\Psi_v = \sum_{v'} f_{\Phi\Psi}(v'; v)\Phi_{v'}. \tag{4}$$

The coefficients in this expansion we shall term the hybrid matrix elements of f, as they differ from ordinary matrix elements in that the wave function on the left belongs to a different set of orthogonal functions from those on the right. The ordinary elements correspond to the special case $\Psi = \Phi$. On multiplication of (4) by $\Phi_{v''}$ and integration throughout the domain of r, we see, using (3), that

$$f_{\Phi\Psi}(v''; v) = \int \Phi_{v''}^* f\Psi_v dr. \tag{5}$$

Let $\Theta_v(r)$ be still a third set of normalized orthogonal functions. The important property of the hybrid elements is that they obey the following law of multiplication

$$(fg)_{\Theta\Psi}(v''; v) = \sum_{v'} f_{\Theta\Phi}(v''; v')g_{\Phi\Psi}(v'; v). \tag{6}$$

To prove (6), note that $fg\Psi_v(r)$ can be expressed equally well as

$$\sum_{v''}(fg)_{\Theta\Psi}(v''; v)\Theta_{v''}(r), \tag{7}$$

or as

$$f\sum_{v'}g_{\Phi\Psi}\,\Phi(v';\,v) = \sum_{v',\,v''} f_{\Theta\Phi}(v'';\,v')g_{\Phi\Psi}(v';\,v)\Theta_{v''}(r). \qquad (8)$$

The result (6) follows immediately on comparing coefficients in (7) and (8). Besides the above multiplication law, the hybrid matrix elements obviously obey the ordinary elementary addition law. Incidentally, these elements for $f = 1$ are not the ordinary Christoffel symbols $\delta_v^{v'}$ since Ψ and Φ are not orthogonal, but do have the property that

$$\sum_{v'}1_{\Theta\Phi}(v'';\,v')1_{\Phi\Psi}(v';\,v) = \delta_v^{v''}.$$

As we have agreed to disregard the rotational factor, the total wave function of the molecule is approximately the product of an electronic wave function $U(x_1, \ldots z_f, r)$ and a vibrational one $R(r)$. Here R is a function only of the inter-nuclear distance r, while U is a function of the Cartesian coördinates of the electrons, measured in a system of reference fixed relative to the nuclei, and also involves r as a parameter. As the electronic and nuclear variables are not rigorously separable in the Schroedinger equation, this resolution of the wave function into electronic and vibrational factors is not exact, but is a good approximation if the vibrational distortion is not too large. It permits us to resolve the total energy W_{nv} into electronic and vibrational parts, so that

$$W_{nv} = W(n) + W_n(v), \qquad (9)$$

where $W(n)$ is the energy for a system in which the nuclei are at rest at the equilibrium distance appropriate to the state n, and $W_n(v)$ is the vibrational energy measured relative to an origin at this equilibrium position. By the Schroedinger-Eckart rule, the elements of any function f are given by[8]

$$f(n'v';\,nv) = \int \ldots \int \int U_{n'}^* R_{n'v'}^* f\, U_n R_{nv}\, dx_1 \ldots dz_f\, dr. \qquad (10)$$

If we omit the vibrational wave factors and integrate over the electronic coördinates, we thereby define a function of r

$$f_{n'n}(r) = \int \ldots \int U_{n'}^* f\, U_n\, dx_1 \ldots dz_f, \qquad (11)$$

which of course involves the initial and final electronic quantum numbers n', n as parameters. We shall write in the electronic quantum numbers as subscripts whenever they appear as parameters in the vibrational problem. Eqs. (5, 10, 11) show that a complete matrix element is a hybrid matrix element in which $f_{n'n}(r)$, $R_{n'v}$, R_{nv} now play the same roles as $f(r), \Phi_v, \Psi_v$ in the notation used in connection with Eqs. (3–5). The rule (6) shows that

$$(f_{n''n'}\, g_{n'n})(v'';\,v) = \sum_{v'}\, f_{n''n'}(v'';\,v')g_{n'n}(v';\,v), \qquad (12)$$

which is not to be confused with the ordinary law of complete matrix multiplication in which the summation over the intermediate states is with respect to both n and v, and so includes all possible electronic levels, whereas in (12) it includes only the vibrational states of one particular electronic level. It is to be understood that for this reason an element (v'', v) of $f_{n''n'} g_{n'n}$ is not the same as the corresponding element of $(fg)_{n''n}$.

Proof That Only Small Raman Displacements in the Vibrational Quantum Number Are Possible.—After the mathematical preliminaries, this proof is quite simple. In view of (9) and the significance of the states a, b, c in the more explicit notation, the Bohr frequency condition may be written as follows:

$$h\nu(ab) = W(n_0) + W_{n_0}(v_0) - W(n) - W_n(v'),$$
$$h\nu(bc) = W(n) + W_n(v') - W(n_0) - W_{n_0}(v''). \qquad (13)$$

Let us substitute (13) in (2), and for simplicity sum until further notice over only the intermediate states belonging to one particular electronic level. As the vibrational energy is small compared to the denominators in (2), we may expand (2) as a power series in $W_n(v')$, thereby bringing $W_n(v')$ in the numerator rather than denominator. Similar expansions in $W_{n_0}(v)$ and $W_{n_0}(v'')$ prove unnecessary, as they are constant with respect to the summation. We thus find for the part of (2) resulting from the intermediate level n

$$\alpha \sum_{v'} \left\{ [A^{-1} - A^{-2} W_n(v') + A^{-3} W_n(v')^2 + \ldots] [P(n_0v; nv')Z(nv'; n_0v'')] \right.$$
$$\left. - [B^{-1} + B^{-2} W_n(v') + B^{-3} W_n(v')^2 + \ldots] Z [(n_0v; nv')P(nv; n'_0v'')] \right\},$$
where   (14)

$$\alpha = \tfrac{1}{2} E e^{2\pi i [\nu_0 + \nu(ac)]t}, \qquad A = h\nu_0 + W(n) - W(n_0) - W_{n_0}(v''),$$
$$B = h\nu_0 + W(n_0) + W_{n_0}(v) - W(n).$$

We have included only terms of the first and second orders in $W_n(v')$, but incorporation of higher orders would occasion no difficulty and would not affect our conclusions. Now the $W_n(v')$ are the diagonal matrix elements of the Hamiltonian function H_{nn} for the vibrational problem of the state n, while the non-diagonal elements are zero as the energy is a diagonal matrix. Hence the first part of (14) can be written

$$\alpha \sum_{v', v^{III}} \left\{ P_{n_0n}(v; v')(A^{-1} - A^{-2} H_{nn} + A^{-3} H_{nn}^2)(v'; v^{III}) Z_{nn_0}(v^{III}; v''). \right.$$
$$(15)$$

Here we have used the notation $P_{n_0n}(v; v')$ rather than $P(n_0v; nv')$, etc., in order to conform to the usage in Eq. (12). We henceforth do not bother to write out the terms arising from the second part of (14), as the manipulation of these terms is similar to that of those from the first part, and can be supplied by the reader. The hybrid multiplication law (6) or (12)

when extended to a triple rather than double product, and use of formula (5) shows that (15) is the same as

$$\alpha \int R_{n_0v}^* \{ P_{n_0n}(A^{-1} - A^{-2}H_{nn} + A^{-3}H_{nn}^2) \angle_{nn_0} \} R_{n_0v''} \, dr. \quad (16)$$

Here the P_{n_0n}, etc., are constructed in the fashion (11) by integrating only over the electronic coördinates, and H_{nn} is the operator

$$H_{nn} = \frac{1}{2M} \left(\frac{h}{2\pi i} \right)^2 \frac{\partial^2}{\partial r^2} + V_n(r),$$

corresponding to the vibrational problem of the state n. The important thing is that in (16) the summations over v', v^{III} have been entirely eliminated. To evaluate (16) exactly it would be necessary to know the vibrational potential energy function $V_n(r)$ for the excited or intermediate level n, but the vibrational wave functions R_{nv} for this level are no longer required. Only those R_{n_0v}, $R_{n_0v''}$ of the normal level are needed. The dependence of the factors P_{n_0n}, $\angle_{nn_0}$ on r is also required, and is in general not known in detail. We may, however, expand these expressions as power series in $(r - r_0)$ if the vibrational excitation in either of the states n_0v or n_0v'' is small. For then either R_{n_0v} or $R_{n_0v''}$ is vanishingly small except in the vicinity of the equilibrium value r_0 of the inter-nuclear distance for the state n_0. This condition is presumably met in the initial state n_0v, as the concentration of molecules in excited vibrational states is usually negligible under ordinary conditions of temperature, etc. The expansion of (16) takes the form

$$\alpha \int R_{n_0v}^* \{ [a + b(r - r_0) + c(r - r_0)^2 + \ldots][A^{-1} - A^{-2}H_{nn} + A^{-3}H_{nn}^2] \\ [g + h(r - r_0) + i(r - r_0)^2] \} R_{n_0v''} \, dr. \quad (17)$$

Since the equilibrium distance r_n for the state n is not the same as that r_0 for the state n_0, the expansion of the potential energy for the state n will contain constant and linear terms in $r - r_0$, whereas the expansion of that for the state n_0 will commence with quadratic terms. Hence the expansions of the vibrational Hamiltonian functions for these two states are, respectively, of the form

$$H_{nn} = \frac{1}{2M} \left(\frac{h}{2\pi i} \right)^2 \frac{\partial^2}{\partial r^2} + d + e(r - r_0) + f(r - r_0)^2,$$

$$H_{n_0n_0} = \frac{1}{2M} \left(\frac{h}{2\pi i} \right)^2 \frac{\partial^2}{\partial r^2} + f_0(r - r_0)^2.$$

Subtraction of these two expressions yields us a formula

$$H_{nn} = H_{n_0n_0} + d + e(r - r_0) + (f - f_0)(r - r_0)^2 + \ldots \quad (18)$$

for H_{nn} which can be substituted in (17) and which is especially convenient because it does not involve the differential operator $(h/2\pi i)^2 \partial^2 \ldots /\partial r^2$. Unless some of the coefficients a, b, etc., happen fortuitously to be particularly small, we can suppose that the terms in (17) having factors $(r - r_0)^0$, $(r - r_0)$, $(r - r_0)^2$ are of rapidly decreasing orders of magnitude, as we supposed at least one of the wave functions R_{nov}, $R_{nov'}$ very small except in the vicinity of r_0. To a sufficient approximation, the vibrational problem of the normal level may be supposed simple harmonic, making R_{nov}, $R_{nov'}$ Hermitian orthogonal functions. Then by the familiar selection rule for the harmonic oscillator, the matrix elements of $r - r_0$ are entirely of the form $\Delta v = \pm 1$, while those of H_{non_0} are, of course, entirely of the type $\Delta v = 0$. (The elements of H_{nn} would not be of this type, as they are diagonal with respect to the R_{nv} rather than R_{nov}; for this reason the substitution of (18) in (17) is necessary.) By the Schroedinger-Eckart rule, the integral (17) is merely a matrix element of the part of the integrand inclosed in parentheses. Hence by the rules for matrix multiplication, the parts of (17) which are of orders $(r - r_0)^0$, $(r - r_0)$, $(r - r_0)^2$ vanish unless, respectively, $\Delta v = 0$, $\Delta v = \pm 1$, $\Delta v = 0$, ± 2. Thus the most intense scattered lines are of the form $\Delta v = 0$, i.e., represent simple Rayleigh scattering, while the most intense Raman lines are those $\Delta v = \pm 1$ whose displacement equals the fundamental of the vibrational frequency. Less intense still are the Raman lines $\Delta v = \pm 2$, whose displacement equals the harmonic of the vibrational frequency, and which are ordinarily far too weak to detect experimentally. This is the desired result. There can be no question of large vibrational transitions, corresponding to passage from one side of the Condon parabola to the other for the intermediate level, as this idea has been dropped out of consideration by using the hybrid multiplication law. Our proof has hitherto involved the restriction of the summation in (2) to one particular intermediate electronic level, but the inclusion of all levels[9,10] merely yields a linear combination of expressions of the type form (17), and so cannot cause large Raman displacements in v.

Polyatomic Molecules.—Essentially the same considerations as in the rest of the paper can be applied to molecules composed of more than two atoms. The main difference is that instead of one vibrational coördinate r, we must utilize several r_1, r_2, . . . which are identical with "normal coördinates" if the vibrations are simple harmonic, and which are associated with different kinds of vibrational quantum numbers v_1, v_2, . . . The same general method as before is applicable. We find that the scattered lines should rank as follows in intensity: first, Rayleigh scattering; second, Raman lines whose displacements equal one of the fundamental vibration frequencies; third, Raman lines whose displacements are either harmonics of a fundamental vibration frequency, or else are "combination fre-

quencies" equal to the sum of two different fundamentals. However, Raman lines which are usually considered to be of the combination type have been reported experimentally without any trace of Raman shifts equal to the fundamental absorption frequencies. In other words, lines which we have ranked third in intensity are apparently found without those we ranked second. Instances in solids or liquids will not be cited, as our theory is primarily for gases. In CO_2 Rasetti[2] finds only Raman shifts of 1284 and 1392 ($\pm$ 10) cm.$^{-1}$ which are not equal to absorption lines, but which are expressible as difference combinations of the two components (3616 and 3720 cm.$^{-1}$) of the doublet absorption band at 2.7μ with that at 4.28μ (2336 cm.$^{-1}$). To account for this anomalous situation two different suppositions (I) or (II) might be made.

(I) One possibility is that the intense Raman lines in CO_2 are fundamentals, and have been misinterpreted as combinations. Eucken's[11] collinear model of the CO_2 molecule does indeed have a fundamental at 1174 cm.$^{-1}$, which Rasetti[12] notes is in the vicinity of his Raman lines, but it is doubtful whether all the details of Eucken's model are tenable. It is perfectly possible for a fundamental to be inactive as an absorption line, but to appear as a Raman line. This will be the case for symmetrical vibrations, which do not create an electrical moment in the molecule in the ordinary (dielectric constant) sense, but which will in general change the magnitude of the moment matrix elements associated with transitions to excited electron levels, and so cause non-vanishing coefficients b, h in Eq. (17). In Eucken's model, for instance, the 1174 cm.$^{-1}$ vibration is inactive in absorption and corresponds to symmetrical displacements of the two O nuclei relative to the C nucleus at the center, thus merely stretching the molecule without altering its symmetry. The sole Raman displacement which Wood[13] finds in NH_3 vapor corresponds to an observed absorption band at 3μ. The very careful recent analysis of the NH_3 vibration spectrum by Stinchcomb and Barker[14] shows that the 3μ vibration is due to oscillations in the altitude of the molecular pyramid, which has the N nucleus at its vertex and the H nuclei at the corners of its base. Their measurements do not reveal whether the 3μ vibration is a fundamental, but Wood's observation of a 3μ Raman displacement is strong evidence that this vibration is really a fundamental, and it is indeed so classed in Dennison's[15] model of the NH_3 molecule. The non-appearance of the other fundamentals as Raman lines suggests that stretching the altitude of the molecular pyramid distorts the moment matrix elements more than do the other normal modes of vibration.

(II) In the particular[16] case of CO_2 another possibility, for which the writer is indebted entirely to Professor Dennison, is that the Raman displacements observed by Rasetti are not pure vibration lines, but rather a combination of rotation and vibration. In a collinear model the energy

of small oscillations of the C nucleus in the median plane (the perpendicular bisector of the line segment joining the two O nuclei) is proportional to $2n_r + n_\varphi$.[17] Here n_r and n_φ are respectively the radial and azimuthal quantum numbers for motions of the C nucleus in the median plane. Hence the apparent vibrational quantum number is $2n_r + n_\varphi$. Now Kemble and Hill,[3] for instance, have shown that only Raman displacements of only 0 and 2 units are possible in rotational quantum numbers such as n_φ. Hence in the Raman effect $2n_r + n_\varphi$ can be displaced only by an even number of units. In investigations not yet published, Dennison interprets the absorption band of CO_2 at 673 cm.$^{-1}$ as due to a unit change in $2n_r + n_\varphi$. The Raman displacements found by Rasetti are approximately double this, and hence might be interpreted as displacements of 2 units in $2n_r + n_\varphi$. This does not contradict the preceding theory in our paper because n_φ is a rotational rather than vibrational quantum number. It is, however, quite different from the usual rotational quantum number in that its effect on the energy is as large as that of vibrations. This is because of the anomalous collinear character of the CO_2 molecule, in virtue of which the moment of inertia about the axis of figure is very small, in fact, zero when the C nucleus is exactly at its equilibrium position.

[1] A. Smekal, *Naturwissenschaften*, **11**, 873 (1923); **16**, 612 (1928); H. A. Kramers and W. Heisenberg, *Zeits. Physik*, **31**, 681 (1925); M. Born, *Naturwissenschaften*, **16**, 673 (1928); A. Sommerfeld, *Atombau und Spektrallinien—Wellenmechanischer Erganzungsband*, p. 203; R. M. Langer, *Nature*, **123**, 345 (1929); G. H. Dieke, *Ibid.*, **123**, 564 (1929).

[2] F. Rasetti, *Nature*, **123**, 205 (1929); *Proc. Nat. Acad. Sci.*, **15**, 234 and 515 (1929).

[3] E. C. Kemble and E. Hill, *Ibid.*, **15**, 387 (1929).

[4] The small effect of the pure vibration amplitudes can be demonstrated by the same type of numerical calculation as used by the writer in showing that they do not contribute appreciably to the dielectric constant. See J. H. Van Vleck, *Phys. Rev.*, **30**, 41–44 (1927).

[5] Cf., for instance, Fig. 7 in E. U. Condon, *Phys. Rev.*, **28**, 1182 (1927).

[6] J. Franck, *Trans. Faraday Soc.*, **21**, part 3 (1925); E. U. Condon, *Proc. Nat. Acad. Sci.*, **13**, 462 (1927); *Phys. Rev.*, **32**, 858 (1928).

[7] Manneback has already given a preliminary account of his results, without any of the details of the proof, *Naturwissenschaften*, **17**, 364(1929).

[8] The "weight function" r^2 appearing when the volume element $dv = r^2 \sin \theta \, dr \, d\theta \, d\varphi$ is expressed in polar coördinates can be eliminated by incorporation of a factor r in the vibrational wave function, and so is not included in the integrand of (10).

[9] We tacitly assume that the superposition effects in adding the contributions of the various intermediate electronic levels do not essentially change the conclusions. These effects could cause destructive interference and so be of importance only if the different intermediate levels gave different signs for the coefficients b,h in (17) in such a way that when expressions of the form (17) are summed over all the intermediate levels, the term of the first order in $r - r_0$ disappears. This appears highly unlikely, as probably changing the inter-nuclear distance affects most of the amplitudes in the same direction, so that most of the coefficients b,h, have the same sign. In any event

an exact cancellation of the first order terms would be exceedingly fortuitous (also a remotely possible explanation of the phenomena found by Rasetti in CO_2). Such interference effects might, however, conceivably explain why incident radiations of certain frequencies are more effective than others in exciting particular Raman lines even without any approach to resonance with the frequencies of the atom.

[10] In summing over the various intermediate electronic levels, the case $n = n_0$ in which the intermediate level is identical with the normal level requires special treatment. The first coefficients a, g, in (17) vanish for $n = n_0$ if the molecule is non-polar. Even with a polar molecule, it can be shown that due to cancellation of the first and second half of (2) the result for $n = n_0$ is the same as if a, g were omitted entirely. The lowest non-vanishing term in the integrand then becomes of order $(r - r_0)^2$. For this reason Raman displacements $\Delta v = \pm 2$ can here, unlike the usual case of excited intermediate levels, be expected to be comparable with $\Delta v = \pm 1$. If, however, the motion is simple harmonic (but not necessarily isotropic, so that the normal coördinates need not be orthogonal) all the Raman displacements arising from intermediate terms of the form $n = n_0$ vanish, as it is readily seen that in this particular case the first and second halves of (2) cancel. This unusual behavior in the case $n = n_0$ does not affect our conclusion because we have already mentioned near the beginning of the paper that in the summation the normal intermediate states make a very small contribution compared to the excited intermediate states, at least in gases. It is conceivable, however, that the amplitudes of pure vibration become more important in solids.

[11] A. Eucken, *Zeits. Physik*, **37**, 714 (1926).

[12] F. Rasetti, *Nature*, **123**, 757 (1929); cf. also P. N. Ghosh, *Ibid.*, **124**, 92 (1929).

[13] R. W. Wood, *Phil. Mag.*, **7**, 744 (1929).

[14] G. A. Stinchcomb and E. F. Barker, *Phys. Rev.*, **33**, 305 (1929); E. G. Barker, *Ibid.*, **33**, 684 (1929).

[15] D. M. Dennison, *Phil. Mag.*, **1**, 195 (1926).

[16] A. S. Gavesan and S. Venkateswaran report results on CS_2 similar to those of Rasetti on CO_2 in that the prominent Raman lines are different from the important, presumably fundamental, absorption lines. Dielectric constant data show that CS_2 is non-polar, or at least nearly so, so that it may be collinear, in which case the same theory can be used for CS_2 as for CO_2. *Nature*, **124**, 57(1929).

[17] Cf. Sommerfeld, *Atombau*, 4th Ed., p. 789, Eq. (29).