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Production of Infrared Spectra with Electric Fields

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A substance in a strong electric field acquires a new infrared spectrum owing to changes in the selection rules. The spectrum is governed by matrix components of the molecular polarizability and hence has the same intensity rules as the Raman effect.

IT IS well known from experience and from the theory of the Stark effect in atomic spectra that electric fields break down selection rules which apply to the atom when not in an electric field. It is natural therefore to suppose such effects might occur in molecular spectra with the consequence that nonpolar molecules like H_2 which have no infrared absorption would become absorbing when placed in a strong electric field. This question is given consideration in the following paper.

For a molecule the matter can be simply considered in terms of two properties: the molecular polarizability and the electric moment. The former is a tensor α_{ij} whose components have fixed values relative to a coordinate system fixed in the molecule. These values are functions of the coordinates fixing the nuclear configuration of the molecule. The electric moment is a vector M_i whose components are likewise most naturally taken in a coordinate fixed in the molecule and which are also functions of the nuclear coordinates of the molecule. The ordinary infrared spectrum of the molecule is determined by the matrix components of the electric moment M_σ referred to axes fixed in space. Suppose *1*, *2*, *3* are the unit vectors along which the axes $i=1, 2, 3$ are taken and that the orientation of these relative to an $(i\,j\,k)$ system fixed in space is specified by Eulerian angles θ, ϕ, ψ, then, if M_σ specifies a component of M in the new system

$$M_\sigma = a_{\sigma i} M_i \tag{1}$$

(using summation convention on double indices). Since the $a_{\sigma i}$ are functions of Euler's angles and the M_i are functions of the internal nuclear coordinates these electric moment components are functions of the vibration and rotation coordinates of the nuclear motion.

To find the infrared spectrum we have to calculate the matrix of the M_σ relative to the stationary states of the motion in the usual way. Letting j, m, λ be the quantum numbers of the rotational motion and writing n shortly for the ensemble of the vibrational motion's quantum numbers we have, for the eigenfunction of the molecule's nuclear state,

$$\psi(n, j, m, \lambda) = F_{\theta\phi\psi}(j, m, \lambda) G_q(n, j, m, \lambda) \tag{2}$$

where F and G are functions of the coordinates indicated as subscripts. F will be the rotator eigenfunctions of the unsymmetrical top in general but may be in special cases the simpler ones for the symmetrical top or even, for straight-line molecules, for the simple rotator. We neglect complicated cases of coupling of rotation and vibration motions. Because of the form of (1) and (2) the matrix components become

$$(n, j, m, \lambda \,|\, M_\sigma \,|\, n'j'm'\lambda' \,| = \int \overline{F}(jm\lambda) a_{\sigma i} F(j'm'\lambda') \cdot \int \overline{G}(njm\lambda) M_i G(n'j'm'\lambda') \quad (3)$$

The first factor is simply the matrix components of the direction cosines which transform from the rotating to the fixed coordinate system and so can be calculated once and for all for the various simple cases, like the simple rotator and the symmetrical top. The probabilities for transitions by emission or absorption of light are given in the usual way by the squared absolute magnitudes of the matrix components in (3). This is the ordinary infrared spectrum.

Now let us consider the behavior of a molecule with regard to radiation when it is in a constant electric field of components, E_σ. It now has an induced electric moment which we call P_σ to distinguish from M_σ, the permanent electric moment. We shall have

$$P_\sigma = \alpha_{\sigma\tau} E_\tau \quad (4)$$

where $\alpha_{\sigma\tau}$ represents the components of α in the fixed coordinate system. By the tensor transformation law we have

$$\alpha_{\sigma\tau} = a_{\sigma i} a_{\tau j} \alpha_{ij}. \quad (5)$$

The new radiative transitions which the molecule may undergo while in the electric field are given by the matrix components of P_σ just as those in the absence of the field are given by the matrix of M_σ. Of course the ordinary infrared spectrum due to M_σ will be present perhaps with very small shifts due to a small Stark effect shift of the levels. The levels in the field are altered by the amount appropriate to the energy of an induced dipole in the field, i.e., by $-\frac{1}{2}P_\sigma E_\sigma$. The level with quantum numbers (n, j, m, λ) is therefore altered by the appropriate diagonal matrix element of this quantity, $(njm\lambda \,|\, -\frac{1}{2}P_\sigma E_\sigma \,|\, njm\lambda)$. We are not as much interested in such small shifts as we are in the new transition possibilities.

The matrix components of P_σ are evidently

$$(njm\lambda \,|\, P_\sigma \,|\, n'j'm'\lambda') = \int \overline{F}(jm\lambda) a_{\sigma i} a_{\tau j} F(j'm'\lambda') \cdot \int \overline{G}(njm\lambda) \alpha_{ij} G(n'j'm'\lambda') \cdot E_\tau \quad (6)$$

The important point is that the selection rules for radiation associated with P_σ will be quite different from those for that due to M_σ for they depend on quite different characteristics of the molecule. As far as rotation is concerned however we can see immediately what the selection rules are for this induced spectrum in terms of those for the ordinary spectrum, because of the form of the part of (6) that depends on the $a_{\sigma i}$. By the rules of matrix multiplication,

$$(jm\lambda \mid a_{\sigma i}a_{\tau i} \mid j'm'j') = (jm\lambda \mid a_{\sigma i} \mid j''m''\lambda'')(j''m''\lambda'' \mid a_{\tau j} \mid j'm'\lambda'),$$

which expresses the rotational factors of the new spectrum's matrix components in terms of those of the usual spectrum.

So far as rotation levels are concerned the transitions of $(jm\lambda) \rightarrow (j'm'\lambda')$ occurring in the induced spectrum will be those which are related by the property of each combining in the ordinary way with some third state (j'', m'', λ''). For the simple rotator this leads to the rule $\Delta j = \pm 2, 0$ in view of the $\Delta j = \pm 1$ of the usual spectrum. This is the selection rule of the Raman effect.

This last remark has a more deep-lying significance than an accidental coincidence, for on looking back over the work we see that the ideas involved are exactly those of Placzek's theory of the Raman effect. He calculates[1] the matrix components of the electric polarizability to get at the intensities and selection rules of the Raman effect. There the induced moment is due to the electric vector of the light wave, here it is due to the steady applied electric field. The induced spectrum we are describing is therefore what might be called the limit of the Raman effect as the frequency of the exciting light tends to zero. It has the same selection rules as the Raman effect.

When the Raman effect was first discovered it was assumed that it would be simply the usual infrared spectrum moved up into the visible part of the spectrum by combination with the frequency of the scattered light. This erroneous view was soon corrected by the facts and by a closer examination of the consequences of the Kramers-Heisenberg theory. This paper however points out how we can do the converse of the original view, namely put the Raman spectrum down into the infrared simply by letting the exciting light frequency tend to zero, it thus becoming an electrostatic field.

The connection with the Raman effect seems also to give a possibility of estimating the possibility of obtaining the induced spectrum in the laboratory. The integrated absorption coefficient over line width $\int \alpha d\nu$ is connected with the number of molecules in unit volume in the lowest state N_1 and the spontaneous transition probability A_{21} by the relation[2]

$$\int \alpha d\nu = N_1(c^2/8\pi\nu)A_{21}.$$

Using the relation of A_{21} to electric moment matrix components we have

$$\int \alpha d\nu = N_1(8\pi^3/3h^2)(h\nu/c) \mid P \mid ^2$$

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[1] Placzek, Zeits. f. Physik **70**, 84 (1931). Actually Placzek omits consideration of the rotational motion of the molecule. The writer worked out the above formulation including rotation last spring and would have calculated it through in detail but for the fact that W. V. Houston reported this problem at the Pullman meeting of the American Physical Society. His calculations are to be published soon according to what I have learned from his associate Mr. C. M. Lewis who is also a visitor at Massachusetts Institute of Technology this summer.

[2] Tolman, Phys. Rev. **23**, 693 (1924).

where P is written shortly for the matrix component in question. It is known that easily observable absorption is obtained say in HCl with $P \sim 10^{-19}$ and $N_1 \sim 10^{19}$ that is with a product of the order $N_1 P^2 \sim 10^{19}$. The polarizability of molecules is of the order 10^{-24} cm^3 and so if we use a liquid or a solid to make $N_1 \sim 10^{22}$ cm^{-3} and a field of 30,000 volts,cm $= 10^2$ e.s.u., we can obtain a product $N_1 P^2 \sim 10^{-22}$ which is still but 10^{-3} of that in HCl. Nevertheless, by use of long tube lengths it might be possible to observe the induced absorption.

One could use a long absorption cell with long condenser plates, applying the field with a high-potential transformer. The alternations of the potential would make no difference since their only effect would be to impress the alternation frequency on the spectrum which would be negligible in spectroscopic units.