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The Relative Intensities of Raman Spectral Bands*

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Received May 20, 1972

A simple method of relating the intensities in a Raman spectrum to bond properties is described. For molecules with high symmetry explicit relationships may be derived.

There is no great difficulty in giving a simple explanation of the factors governing the relative intensities of the vibrational bands which appear in an infrared spectrum. In the simplest model, for each change in bond length or bond angle consequent upon a vibration of a molecule there is a corresponding dipole moment change which can be represented by a vector. It is the resultant of the appropriate combination of these vectors which is related to the intensity of an infrared absorption band. In contrast, the factors which determine the relative intensities of Raman spectral bands are less widely appreciated. Many books simply state that Raman intensities are determined by the magnitudes of the elements of a derived polarisability tensor, but give little further explanation of the phenomenon. In the present paper we present an approach wich parallels that commonly given for infrared intensities. In particular we present a simple physical model which in suitable cases, readily leads to expressions for relative intensities of Raman spectral bands.

We consider in detail the vibrations of an octahedral molecule, ML_6, and the Raman bands corresponding to the M-L bond stretching vibrations. It is readily shown using elementary group theory that the six independent ML stretching vibrations combine in the O_h point group to give group vibrations of symmetry species A_{1g}, E_g, and T_{1u}. Of these, only the first two modes are Raman active and it is with their relative intensities that we concern ourselves.

Each M-L bond in the molecule is polarisable. Its polarisability may be represented by a tensor. This tensor, which may be depicted by something shaped like a football (as shown in Figure 1), may be described by an equation of the form $ax^2 + by^2 + cz^2 =$ constant, where x, y and z are principal axes (if we chose coordinate axes in arbitrary, but mutually perpendicular directions, terms in xy, yz and zx appear). If we were to place the M-L bond - hypothetically(!) - inside a large parallel plate condensor and apply a potential across the plates, then the dipole induced within the M-L bond is not, in general, along the same axis as the applied electric field because the electron density in the bond is more polarisable in some directions than in others, the dipole is induced along an axis which is inclined from the electric field axis towards the direction of greatest polarisability (Figure1). If the M-L bond length is now altered (as in the vibrations we are considering) the bond polarisability tensor will, in general, also change.

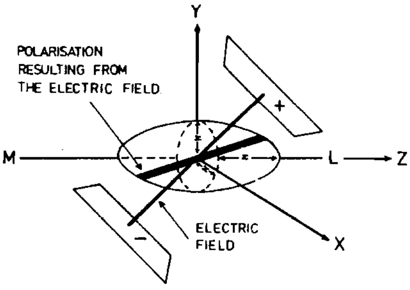

Figure 1.

The difference between the two tensors appropriate to different M-L bond lengths may also be represented by a tensor. It does not necessarily follow, however, that this tensor, the derived bond polarisability tensor, can be represented as in Figure 1. When a bond length is changed the bond polarisability in a particular direction may either increase or decrease and, in general, a derived bond polarisability tensor may have both positive and negative elements *i.e.* may be represented by negative as well as positive regions. It is with derived bond polarisabilities that we are concerned since they determine the intensity of a Raman spectral band.

In the particular case of an octahedral complex ML_6, wherein each bond tensor is associated with a four-fold rotational axis, the tensor has cylindrical symmetry and it is only necessary to specify the magnitude of two quantities in order to define it. This situation is indicated in Figure 1 where x and z are the two quantities which have to be specified for in this case, $y=x$.

The forms of the A_{1g} and E_g M-L stretching vibrations of an ML_6 molecule are given by the equations

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(*) Presented at the 3rd International Symposium sponsored by Inorganica Chimica Acta, Venice, 1970.

$$\psi(A_{1g})=\frac{1}{\sqrt{6}}(A+B+C+D+E+F)$$

$$\psi(E_g,x^2-y^2)=½(B-C+D-E)$$

$$\psi(E_g,\frac{2z^2-x^2-y^2}{\sqrt{3}})=\frac{1}{2\sqrt{3}}(2A-B-C-D-E+2F)$$

In these equations A,B,C,D,E, and F represent extensions of the M-L bonds to ligands L_A, L_B, L_C, L_D, L_E, and L_F in Figure 2. We now obtain the tensors appropriate to the changes in molecular polarisability when these vibrations occur. We do so by expressing them as sums of derived bond tensors which we have already discussed, a method introduced by Wolkenstein.[1,2,3,4] Implicit is the independence of the derived bond tensor components *a* and *b*, corresponding, respectively, to *x* and *z* of the bond polarisability tensor and to emphasise this we represent derived bond tensors as indicated in Figure 3 (note that the signs of *a* and *b* are unspecified). The conventional primes on the *a* and *b* (indicating that they are related to a derived polarisability) are for convenience, omitted in the present paper.

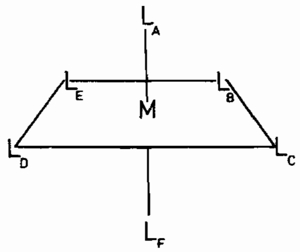

Figure 2.

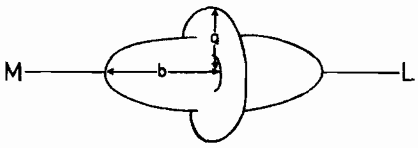

Figure 3.

The change in molecular polarisability corresponding to the A_{1g} normal mode is the sum of bond derived polarisabilities of the form indicated by $\psi(A_{1g})$ A pictorial representation of the bond contributions to the molecular derived polarisability change consequent upon an A_{1g} vibration is shown in Figure 4. We have to combine these components appropriately. However, before we do this we consider some symmetry aspects of the problem in order to simplify our discussion.

It may be shown group theoretically that only molecular vibrations which transform like a product of coordinate axes may be Raman active. Of the infinite possible linear combinations of products of pairs of the molecular coordinate axes (xx, yy, zz, xy, xz and yz) the only type of combination which has A_{1g} symmetry is of the form (xx+yy+zz). As a consequence of this only the xx, yy and zz elements of the molecular derived polarisability tensor associated with the A_{1g} M-L stretching mode can be non-zero (we follow the choice of coordinate axes shown in Figure 2). Further, each of these three diagonal terms must be equal in both magnitude and sign (since xx, yy and zz appear with identical coefficients in their A_{1g} combination). We show how to obtain the zz component; the xx and yy components are similarly obtained. Reference to Figures 2 and 4 shows that M-L_A and M-L_F each have bond derived polarisability tensor z axes coincident with the molecular z axes so that each make a contribution to this molecular derived polarisability tensor element of $\frac{b}{\sqrt{6}}$. Similarly, each of the remaining four bond-derived polarisability tensors contribute $\frac{a}{\sqrt{6}}$ to this molecular tensor element. Summing these we conclude that the zz element has the magnitude $\frac{1}{\sqrt{6}}$ (2b+4a).

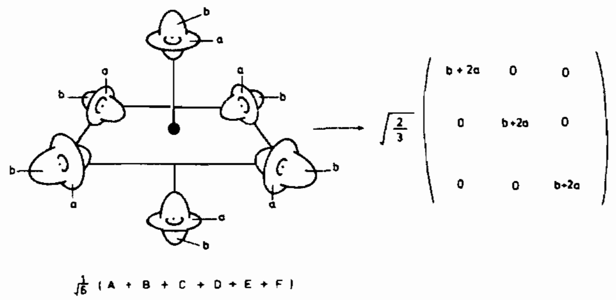

Figure 4.

We now show that there is no nett molecular derived polarisability change associated with the M-L stretching vibration of symmetry species T_{1u}. For the T_{1u} vibration, $\psi(T_{1u},z) = \frac{1}{\sqrt{2}}$ (A–F) and the bond derived polarisability tensor contributions from M-L_A and M-L_F are $\frac{b}{\sqrt{2}}$ and $-\frac{b}{\sqrt{2}}$, respectively, giving a molecular derived zz tensor element of zero. Similarly, the bond contributions to the xx and yy elements cancel. Morever, because of the coincidence of molecular and bond axes, there are no non-zero off-diagonal molecular derived polarisability elements.

We now consider the M-L stretching vibrations of symmetry species E_g. We consider the two vibrations separately. That E_g vibration which transforms as x^2-y^2 is shown diagrammatically in Figure 5. The form of the coresponding derived molecular polarisability tensor expressed in terms of bond components is shown in Figure 6. The signs of the relative contributions of the derived polarisability tensor elements are derived from those of the corresponding

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(1) M. Wolkenstein, *J. Exp. and Theor. Phys.*, *11*, 642 (1941).
(2) M. Wolkenstein, *J. Phys.*, *5* ,185 (1943).
(3) M. Eliashevich and M. Wolkenstein, *J. Phys.*, *9*, 101 (1945).
(4) M. Eliashevich and M. Wolkenstein, *J. Phys.*, *9*, 326 (1945).

M-L stretching motions in the above equation for $\psi(E_g, x^2\text{-}y^2)$. The explicit form of the molecular derived polarisability tensor is obtained in a similar way to that of the A_{1g} case. Consequently, the zz component is equal to $\frac{1}{2}(a\text{-}a+a\text{-}a) = 0$. The xx component, however, is non-zero and is equal to $\frac{1}{2}(2b\text{-}2a)$ Similarly, the yy component is equal to $\frac{1}{2}(-2b+2a)$. Again, all off-diagonal terms are zero. We note that the two non-zero diagonal terms are equal in magnitude but opposite in sign, just as expected for a vibration transforming as $x^2\text{-}y^2$. The second component transforms as $2z^2\text{-}x^2\text{-}y^2$. The bond contributions to the molecular derived polarisability tensor are shown in Figure 7, wherein the contributions from the ligands L_A and L_F are twice the size and opposite in sign to the individual contributions from ligands L_B, L_C, L_D and L_E. Combing the components gives a zz component of $\frac{1}{2\sqrt{3}}(4b\text{-}4a)$ and xx and yy components of $\frac{1}{2\sqrt{3}}(2a\text{-}2b)$. Once again all off-diagonal elements are zero. It is to be noted that each of the two E_g vibrations give rise to tensors which contain only multiples of $(b\text{-}a)$.

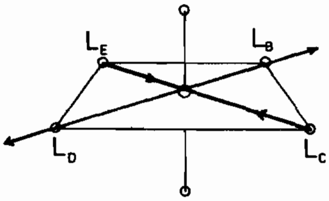

Figure 5

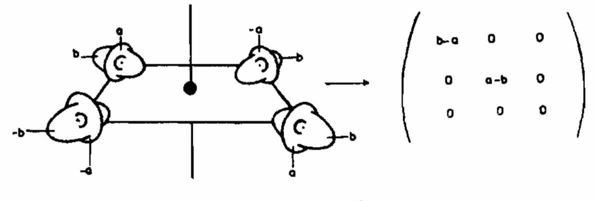

Figure 6.

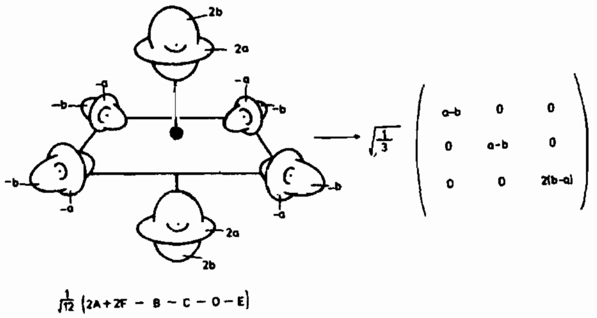

Figure 7.

The expressions which we have derived above for the molecular derived polarisability tensor elements are appropriate to one molecule held fixed in a set of Cartesian coordinate axes. These axes might, for example, be those determined by the geometric design of a Raman spectrometer and by the direction and polarisation of an incident laser beam. In practice, however, for polycrystalline, liquid and gaseous samples we are dealing with a multitude of molecules randomly oriented with respect to the laboratory axes. Before using the molecular polarisability expressions we have derived we must allow for this random orientation. The method of doing this is given by Wilson, Decius and Cross.[5] We take up the argument from equation (24) of Section 3-6 of their text. This equation is

$$I_T(\text{obs} \perp) = \frac{16\pi^4\nu^4}{c^4} N I_o \frac{45\alpha^2+7\beta^2}{45} \tag{1}$$

in which α^2 is equal to $\frac{1}{9}(xx+yy+zz)^2$ and β^2 is equal to $\frac{1}{2}[xx\text{-}yy)^2+(yy\text{-}zz)^2+(zz\text{-}xx^2]$. Let us consider the intensity of the A_{1g} band. For this β is equal to zero because $xx = yy = zz$. In this case equation (1) reduces to

$$I_T^{A1g}(\text{obs} \perp) = \frac{16\pi^4\nu^4_{A1g}}{c^4} N I_o \alpha^2$$

which on subsituting for α^2 becomes

$$I_T^{A1g}(\text{obs} \perp) = \frac{32\pi^4\nu^4_{A1g}}{3c^4} N I_o (b+2a)^2$$

In the case of E_g vibrations there are two components, each of which contributes separately to the observed intensity. For these vibrations α is equal to zero because the sum of tensor elements along the leading diagonal of each of the E_g derived tensors is equal to zero. For the E_g vibrations it is the term in β^2 which gives rise to the observed intensity. For the $x^2\text{-}y^2$ vibration the contribution to the intensity is

$$I_T^{E_g(x^2-y^2)}(\text{obs} \perp) = \frac{336\pi^4\nu^4 E_g}{45c^4} N I_o (b-a)^2$$

and is equal to that for the $2z^2\text{-}x^2\text{-}y^2$ component.

Adding the two contributions we arrive at the final expression for the intensity of the E_g mode which is

$$I_T^{E_g}(\text{obs} \perp) = \frac{224\pi^4\nu^4 E_g}{15c^4} N I_o (b-a)^2.$$

The expressions for the intensities of the A_{1g} and E_g modes are simplified if we consider their ratio, given by the following expression,

$$\frac{I_T^{A1g}}{I_T^{Eg}}(\text{obs} \perp) = \frac{5}{7}\frac{(b+2a)^2}{(b-a)^2},$$

where we have set $\nu_{A1g} = \nu_{E1g}$ (note that ν refers to

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[5] «Molecular Vibrations», E.B. Wilson, J.C. Decius, and P.C. Cross. McGraw-Hill, New York, 1955.

the frequency of the scattered light, not the frequency of the vibration).

In Figure 8 we plot the ratio ($I_T^{A_{1g}}/I_T^{E_g}$) (obs $\perp$) against x, where x is equal to $\frac{a}{b}$. In Figures 9 and 10 we give two examples of spectra of octahedral molecules showing A_{1g} and E_g bands. In the two cases the ratio ($I_T^{A_{1g}}/I_T^{E_g}$) (obs $\perp$) are 0.14 and 3.0 respectively. From Figure 8 it is evident that in the first example the value of x must be negative. That is, for this compound, when the CO bonds stretch the polarisability changes are of opposite sign along and across the CO bond axis.[*] For the second example, it is similarly possible to say unambiguously that x is positive. In both cases, however, there is an ambiguity about the actual value of x. For SF_6 x is either 0.3 or 61.7.

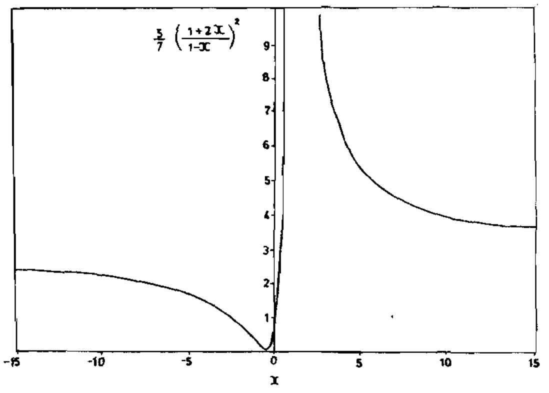

Figure 8.

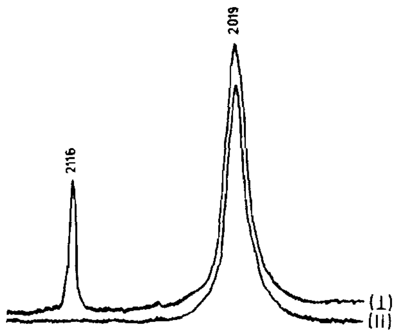

Figure 9.

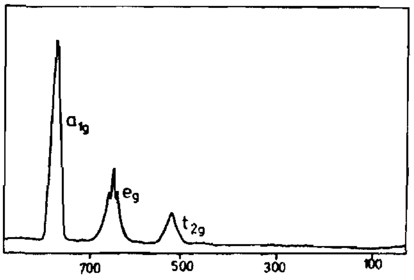

Figure 10.

From chemical properties, it seems probable that in the case of SF_6 the dominant polarisation changes will be along the bond axis. If this is so then the value of x = 0.3 is the more appropriate. However, in the case of $Mo(CO)_6$ the possible values are $x = -1.1$ and $x = -4.5$ and either value of x indicates that along the bond axis polarisation changes are less important than those transverse to it. If, as is often asserted, π-bonding effects have a determining role in metal carbonyl vibrational spectroscopy, the value of x = -4.5 may be preferred. On the other hand, if it is held to be more probable that x values all fall in a limited range (as has been suggested by CHANTRY and PLANE)[6] then the value of -1.1 is the more appropriate.

It is not difficult to extend this type of argument to those vibrations which involve changes in bond angles . The main difference is that our derived polarisability tensors have to be associated with bond angle changes and not with bond length changes. That is, they have to be located between bonds and not along them. Such a set appropriate to an octahedron is shown in Figure 11 where, to keep the diagram as simple as possible, we show only four of the total of twelve angle derived polarisability tensors. It is to be noted that we have reoriented the x and y axes compared with those given in Figure 2. This is because the approach which we describe is much easier when the bond or angle derived tensors are oriented along molecular coordinate axes, as opposed to between them. In practice, what we call the xx component using the set of axes in Figure 11 corresponds to the xy component using those of Figure 2.

The only Raman active bond deformation modes of a simple octahedral molecule are of symmetry species T_{2g}. The form of one of these vibrations is shown

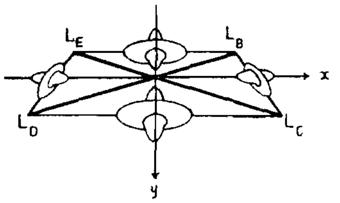

Figure 11.

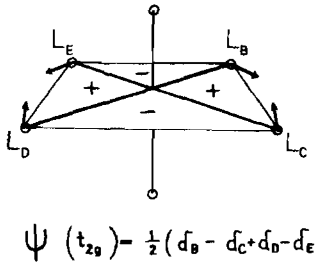

Figure 12.

(*) Here we ignore mixing of the C-O and M-C stretching modes, although this mixing is, strictly speaking, relevant to the discussion.

(6) G.W. Chantry and R.A. Plane, *J. Chem. Phys.*, 33, 634 (1960).

in Figure 12. The T_{2g} molecular derived polarisability is obtained from the set of angle derived polarisability tensors represented in Figure 11 using the phases of Figure 12. The result is indicated in Figure 13, from which it follows that the xx molecular derived polarisability tensor element is $\frac{1}{2}(2c-2d)$. Note that there is an apparent ambiguity here. Had we evaluated the yy element we would have obtained a similar answer. However, each of these correlate with xy of the original coordinate system (xx with xy and yy with -xy) and, in fact, no ambiguity arises. Because of the absence of any other derived polarisability tensor which provides a second relationship between *c* and *d* it is only possible to obtain a measure of the difference between these two quantities in a Raman experiment.

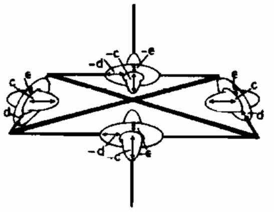

Figure 13.

Our discussions of the vibrations of an octahedral complex were greatly simplified by the fact that one could choose axes sets for each ligand which were both parallel to one another and to the molecular axes, In the more general case this simplification does not exist and it becomes necessary to carry out correct tensor transformations before one can obtain algebraic expressions for molecular derived polarisability changes in terms of bond or angle derived polarisability components. In the present paper we demonstrate that these calculations have a simple pictorial representation. As an example we consider the case of a hypothetical AB_2 molecule of C_{2v} symmetry. An additional complication arises because the bond derived polarisability tensors do not have cylindrical symmetry down one axis (this was also the case for the angle derived polarisability tensors, discussed above). That is, at least three axial quantities, which we shall denote *a, b, c,* are needed in order to define such a bond tensor. Consider the symmetric and antisymmetric A-B stretching vibrations of our AB_2 molecule. Figure 14 gives a suitable representation where we have chosen to indicate the independence of the bond tensor elements *a, b,* and *c* by drawing them in a manner somewhat analogous to that of an atomic orbital.

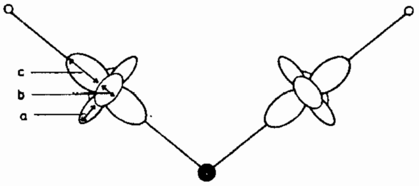

Figure 14.

In order to obtain the molecular derived polarisability change corresponding to the symmetric stretching vibration, we simply combine bond tensors such as those shown in Figure 14. In Figure 15 we show a pictorial representation of this combination. In figure 15a we have assumed that the tensor elements *a* and *b* are of the same sign whilst in Figure 15b we have assumed them to be of opposite sign. The actual shape shown in Figure 15 should not be taken too literally; in practice a more faithful representation may well be closely related to that indicated in Figure 1. In Figures 14 and 15 we present the *c* tensor component rather faintly because it can be seen that its contribution to the total polarisability change is similar in both Figures 15a and 15b.

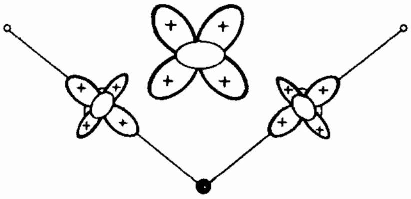

Figure 15(a).

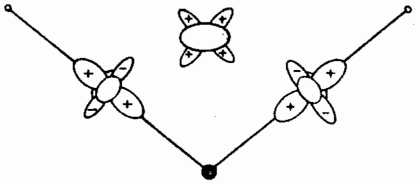

Figure 15(b).

It should be noted that the resultants of he derived bond tensors shown in Figures 15a and 15b have been obtained by a simple addition of their compo-

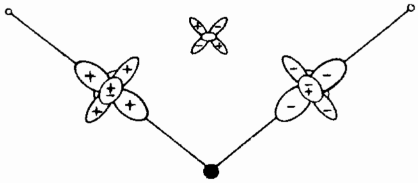

Figure 16(a).

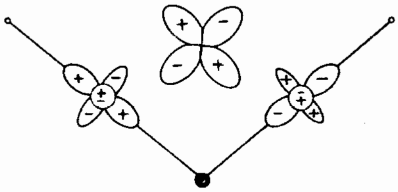

Figure 16(b).

nents. This procedure is sufficient for the present qualitative discussion; it is, strictly, only possible to carry out the addition after the derived bond tensors have been referred to a common (molecular) axis system.

In Figures 16a and 16b we represent the derived polarisability tensors appropriate to the antisymmetric combination of A-B bond stretches. As for Figure 15, Figures 16a and 16b show respectively the cases where *a* and *b* are of the same and of opposite sign. A comparison of Figures 15 and 16 indicates quite clearly that when *a* and *b* are of opposite sign the antisymmetric mode may give rise to the more intense Raman band. This is because in Figures 15b and 16b the latter corresponds to the larger derived polarisability change, as indicated by the larger atomic orbital like function in Figure 16b. Although a relatively uncommon phenomenon, the intensity of the antisymmetric mode is greater than that of the symmetric mode for some compounds containing $M(CO)_2$ groups in the 2000 cm^{-1} region.

Conclusions

In this paper we have attempted to show that it is possible to place a relatively simple interpretation on the intensities of bands observed in the Raman spectra. It must be pointed out, however, that other factors can intervene. For example, the intensity of the scattered radiation is not constant for all scattered wavelengths but has a ν^4 dependence (cf. equation 1). Similarly, the sensitivity of the photomultiplier and the efficiency of the gratings used in the Raman spectrometer are not independent of wavelength. These things would not matter if a double beam Raman instrument were being used but in practice all spectra are obtained on single beam machines. It follows, therefore, that unless one is prepared to make a correction for all of these additional intensity modulating features arguments of the type that we have presented in this paper can only be applied to bands which are relatively close together in a spectrum.