Analysis of the effect of pressure on optical spectra

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Curie, Berry, and Williams have recently published a theory of the effect of pressure on the frequency of optical-absorption emission lines in solids. They argue that our earlier work (with Frank) as well as that by Henry, Schnatterly, and Slichter is wrong. In this paper we analyze and compare the methods of calculation. As we explain, we believe their calculation necessarily brings into play a hidden variable needed to specify the state of the pressure apparatus. We believe their method causes that variable to change in the optical transition, thereby violating the Franck-Condon principle.

I. INTRODUCTION

The effect of pressure on optical spectra has long been of interest. Together with Frank,[1] we published a paper titled "Optical Versus Thermal Transitions in Solids at High Pressure" in 1972 which we will refer to as DFS. In 1964[2] and 1965[3] Henry, Schnatterly, and Slichter[4] published papers titled "Effect of Applied Fields on the Optical Properties of Color Centers" which dealt with the effect of applied electric or magnetic fields or mechanical stresses. The basic viewpoints of these papers agree with DFS.

Recently Curie, Berry, and Williams (CBW)[5] have calculated the effect of pressure on optical spectra using an approach which differs from that of DFS. They have published several papers giving their result and stating that we are wrong.

These papers contain references to the earlier literature consistent with their approach. We carefully examined their approach and reexamined our own. We concluded that we were correct, and identified what we believe to be a subtle but fundamental error in the approach of CBW.

In this paper, we present an analysis of the effect of pressure on optical spectra in such a form as to point out just where the two groups differ and show that their approach *necessarily* brings into play a hidden variable needed to specify the state of the pressure apparatus. We conclude that their method causes that variable to change in the optical transition, which in our judgement violates the Franck-Condon principle.

In Sec. II we state the problem at issue. In Sec. III we give the Drickamer, Frank, and Slichter calculation. In Sec. IV we outline the CBW calculation and discuss the disagreement. In Sec. V we give a quali-

tative explanation of the reason for the disagreement. In Sec. VI we give a quantitative explanation of the disagreement showing explicitly the hidden variable which accounts for what we believe is their error. Of course, the disagreement is over theory, but CBW discuss experiments to support their viewpoint. In the Appendix we give comments on the experimental situation.

II. PROBLEM AT ISSUE

The physical system under discussion is a solid which possesses a reasonably narrow optical-absorption band arising from an electronic transition from a ground to an excited electronic state. The narrow band might arise from the presence of a foreign atom or of defects (color centers) or, in the case of a molecular solid, a transition from a ground to an excited state of a molecule. The question at issue is what happens to the frequency of the peak of the optical absorption if the solid is subjected to an externally applied pressure p. In all such systems there is for each electronic state an equilibrium volume for the sample. Typically the equilibrium volume of the excited state V_{exc}, differs from the equilibrium volume of the ground state V_{gnd}.

We conclude that application of a pressure produces a frequency shift, $\Delta \nu$ which always contains one term proportional to $p \, (V_{exc} - V_{gnd})$, i.e., linear in pressure, plus another term quadratic in pressure. We find that there is always a linear term when $V_{exc} \neq V_{gnd}$.

CBW conclude that the linear term is missing unless the compressibility of the crystal in the excited state differs from its value in the ground state, a con-

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dition much more restrictive than our own. The problem, then, is to calculate the effect of pressure on the peak of the optical-absorption band.

Certain expressions occur repeatedly throughout this paper. It is therefore well at this stage to point out three well-known relationships which we call Eqs. (1)–(3). Consider a spring with spring constant k. Let a force, F, be applied to stretch the spring. Let x be the amount the spring is stretched. Hooke's law gives the relation between F and x,

$$F = kx \quad . \tag{1}$$

In stretching the spring from an initial stretch x_i to a final stretch x_f, the force does work on the spring W_{if} of amount

$$W_{if} = \int_{x_i}^{x_f} F(x)\,dx \quad , \tag{2}$$

which, using Eq. (1) for $F(x)$, is readily integrated to give

$$W_{if} = \tfrac{1}{2} k \left(w_f^2 - x_i^2 \right) \quad . \tag{3}$$

We may use Eq. (1) to express Eq. (3) alternatively as

$$W_{if} = \tfrac{1}{2} [F(x_f)^2 - F(x_i)^2]/k \quad . \tag{4}$$

We repeatedly use Eqs. (3) and (4) in this paper.

III. DRICKAMER, FRANK, AND SLICHTER APPROACH

A. Calculation of the pressure dependence of the absorption frequency

In the absence of an applied pressure, the calculation of the energy of a solid containing a color center at absolute zero temperature can be done by well-known methods given in the standard texts on solid-state physics. In essence one takes the positions $\vec{R}_i$ of the various atoms as parameters, solves a Hamiltonian for the motion of the electrons, eventually getting the electron wave functions, ψ_a, corresponding to different electronic states of the color center, and the total crystal energy. By varying the $\vec{R}_i$'s one finds the minimum energy for each electronic state. In general, the values of $\vec{R}_i$ which minimize the total crystal energy differ for the different electronic states. Thus the crystal volume in general is different between the ground and an excited electronic state.

For a given electronic state, the total crystal energy increases when the $\vec{R}_i$'s are displaced slightly from their equilibrium values. Since the ions possess mass, a time-dependent displacement of an ion contributes kinetic energy to the total energy of the crystal. The discussion of such small displacements is then a normal-modes problem which may be treated

either as a classical or a quantum-mechanical problem. We treat the problem classically in this paper since the fundamental disagreement at issue can be seen more simply using classical arguments, though it also is found quantum mechanically. The normal-modes problem is solved by finding the proper normal coordinates Q_i which give the displacement of the $\vec{R}_i$'s from their equilibrium values. In general, the Q_i's are linear combinations of the displacements of the $\vec{R}_i$'s from equilibrium. In the most general case, the proper linear combinations differ for the different electronic states. The extra contribution to the total crystal energy resulting from the displacements of the $\vec{R}_i$'s from their equilibrium positions is called the elastic energy. When the solid is in thermal equilibrium at some temperature, T, the elastic vibrations are thermally excited and provide the lattice contribution to the specific heat.

We can illustrate by a particularly simple case in which we consider a system characterized by a single generalized coordinate Q, and a pair of electronic states we label as the ground and excited states. For our problem, we take Q to be the volume change of the crystal from its equilibrium value when the system is in the ground electronic state.

The total crystal energy for the system in the ground electronic state may be written as follows:

$$E_T(\text{gnd}) = E_0 + \tfrac{1}{2} m\dot{Q}^2 + \tfrac{1}{2} k_g Q^2 \quad , \tag{5}$$

where E_0 is the total energy when the atoms are at rest at the position of minimum energy ($Q = 0$), and where m and k_g are coefficients which come from solving the normal-modes problem of the crystal, and may be conveniently thought of as a mass and a spring constant, respectively. The terms involving $\dot{Q}$ and Q are, respectively, the elastic kinetic and potential energies.

If the system is in the excited electronic state, the total energy is

$$E_T(\text{exc}) = E_1 + \tfrac{1}{2} m\dot{Q}'^2 + \tfrac{1}{2} k_e Q'^2 \quad , \tag{6}$$

where Q' represents the displacement of the volume from its value when the lattice vibrations are quiescent. The fact that the compressibility of the solid in general depends on the electronic state of the color center is expressed by the fact that k_e may be different from k_g. The fact that the equilibrium volumes differ for the ground and excited electronic states is expressed by the fact that $Q' \neq Q$. We assume that Q and Q' are related by the equation

$$Q' = Q - \Delta \quad . \tag{7}$$

That is, we assume only *one* normal mode of the ground state is involved in the normal mode of the excited electronic state. Therefore,

$$E_T(\text{exc}) = E_1 + \tfrac{1}{2} m\dot{Q}^2 + \tfrac{1}{2} k_e (Q - \Delta)^2 \quad . \tag{8}$$

Equations (5) and (8) are the harmonic approximations to the total energy of the crystal and are accurate as long as the ions remain close to their equilibrium positions. It is easy to generalize these equations to include many more normal modes, but such a generalization is not necessary for understanding the disagreement between DFS and CBW.

By means of Eqs. (5) and (8) one can analyze many problems. For example, one can apply the equipartition theorem to compute the manner in which thermal excitation changes the average total crystal energy, and thereby calculate the heat capacity. Or, as we show below, one can calculate the optical-absorption frequency as a function of pressure.

Let us first consider the case of zero applied pressure, the one case for which DFS and CBW get the same answer for the frequency of the optical absorption. We consider the system to be in its ground electronic state initially. Let us assume there is negligible thermal excitation of the lattice vibrations so that initially

$$Q = 0, \quad \dot{Q} = 0 \tag{9}$$

and

$$E_T(\text{gnd}) = E_0 . \tag{10}$$

We now shine light on the system producing a transition to the excited electronic state. We know from the Franck-Condon principle that during that transition the ions do not have time to move nor to change their velocities. Therefore, the crystal has $Q = 0$, $\dot{Q} = 0$ immediately after the transition, giving from Eq. (8)

$$E_T(\text{exc}) = E_1 + \frac{1}{2} k_e \Delta^2 . \tag{11}$$

The photon must supply the change in total crystal energy so that subtracting Eq. (10) from Eq. (11) we get

$$h\nu(0) = E_1 + \frac{1}{2} k_e \Delta^2 - E_0 , \tag{12}$$

where $\nu(0)$ means the frequency corresponding to zero pressure.

What happens if we apply a pressure to the system prior to shining the light? The applied pressure compresses the crystal, changing the relative positions of the ions, and therefore changing the total energy of the crystal. Suppose we apply a pressure when the system is in the ground electronic state which causes Q to become Q_a. We assume that the pressure is applied in such a way that we leave the system with $\dot{Q} = 0$. Then Eq. (5) shows that the total crystal energy in the ground state becomes

$$E_T(\text{gnd}, Q_a) = E_0 + \frac{1}{2} k_g Q_a^2 . \tag{13}$$

The term $\frac{1}{2} k_g Q_a^2$ is elastic potential energy which was provided by the work done by the applied pressure in moving Q from 0 to Q_a just as in Eq. (3).

Once again if an optical transition is induced, Q and $\dot{Q}$ do not change during the transition. Therefore, immediately after the transition the crystal finds itself in the excited state with $Q = Q_a$, $\dot{Q} = 0$, giving a total crystal energy of

$$E_T(\text{exc}, Q_a) = E_1 + \frac{1}{2} k_e (Q_a - \Delta)^2 . \tag{14}$$

In the case we are studying, the crystal is not isolated. It is coupled to the apparatus which supplies the pressure. But since Q does not change during the optical transition, the crystal volume does not change, and therefore the pressure reservoir does no work on the crystal during the optical transition. As a result, it is the light quantum which must supply the difference between the total crystal energy before and after the transition.

Using $\nu(Q_a)$ to denote the optical transition frequency in this case, we have

$$h\nu(Q_a) = E_1 + \frac{1}{2} k_e (Q_a - \Delta)^2 - E_0 - \frac{1}{2} k_g Q_a^2 . \tag{15a}$$

$$h\nu(Q_a) = (E_1 - E_0) + \frac{1}{2} k_e \Delta^2$$
$$- k_e Q_a \Delta + \frac{1}{2} (k_e - k_g) Q_a^2 . \tag{15b}$$

Comparing Eq. (15b) with Eq. (12) we see that

$$h\nu(Q_a) - h\nu(0) = -k_e Q_a + \frac{1}{2} (k_e - k_g) Q_a^2 . \tag{16}$$

If we know Q_a, Eq. (16) gives us the shift in optical frequency. More commonly the information we are given is the size of the applied pressure p_a. However, Q_a can be expressed in terms of p_a if we simply recall that an infinitesimal volume change dV produced by an applied pressure, p, does work on the crystal of $-p\,dV$. This work goes into the total crystal energy, so that, recalling that Q stands for a volume change,

$$\frac{\partial E_{\text{tot}}(\text{gnd})}{\partial Q} = -p . \tag{17}$$

which gives us, from Eq. (5)

$$k_g Q = -p . \tag{18}$$

Therefore

$$Q_a = -p_a / k_g . \tag{19}$$

Thus we can express the frequency change explicitly in terms of pressure

$$h[\nu(p_a) - \nu(0)] = + \frac{k_e}{k_g} \Delta p_a + \frac{1}{2} \frac{(k_e - k_g)}{k_g^2} p_a^2 . \tag{20}$$

Equation (20) is the principal result we seek, the effect of pressure on the optical-absorption frequency.

It is this equation, published by DFS, which CBW assert is wrong. The first term on the right is the linear pressure term. According to our analysis the term is present irrespective of the relative size of k_e and k_g. CBW find an expression for the linear term which contains the factor $(k_e - k_g)$. They conclude from their expression that the linear term vanishes when $k_e = k_g$.

The essential aspect of our argument is that if one knows Q and $\dot{Q}$ one knows the total energy of the crystal for each electronic state, the explicit formulas being given by Eq. (5) and (8), and the shift of the optical peak being given by Eq. (16). Note that at no place in Eq. (16) does the pressure appear explicitly.

One way of stating our basic disagreement with CBW is in terms of our Eq. (16). They claim that, in *addition* to the terms we find, in which there is an implicit pressure effect, through Eq. (19) there is an *explicit* pressure dependent term.

B. Conservation of energy under the influence of applied pressure

Equations (13) and (14) apply to instants of time at which $\dot{Q} = 0$. But even in the presence of an applied pressure, p_a, it is possible for Q to be set in vibration about the equilibrium position Q_a. Let us assume the pressure is held constant during the vibration. In such a vibration, the crystal does work (positive or negative) against the applied pressure as Q oscillates. *Therefore the total crystal energy is not constant during the cycle of the oscillation.* In going from one value of Q, which we call Q_i to another value we call Q_f, the crystal does work $p_a(Q_f - Q_i)$ against the source of pressure so that the total crystal energy at Q_i, $E_T(Q_i)$ is related to the corresponding quantity at Q_f, $E_T(Q_f)$, by

$$E_T(Q_i) = E_T(Q_f) + p_a(Q_f - Q_i) \tag{21a}$$

or

$$E_0 + \tfrac{1}{2}m\dot{Q}_i^2 + \tfrac{1}{2}k_g Q_i^2 = E_0 + \tfrac{1}{2}m\dot{Q}_f^2 + \tfrac{1}{2}k_g Q_f^2$$
$$+ p_a(Q_f - Q_i) , \tag{21b}$$

where $\dot{Q}_i$ and $\dot{Q}_f$ are the values of $\dot{Q}$ for $Q = Q_i$ and $Q = Q_f$, respectively.

We can rewrite Eq. (21b) by collecting terms involving Q_i on the left side and involving Q_f on the right side, to get an equation which holds for arbitrary Q:

$$E_0 + \tfrac{1}{2}m\dot{Q}^2 + \tfrac{1}{2}k_g Q^2 + p_a Q = C , \tag{22}$$

where C is a constant, the value of which depends on the initial conditions, i.e., what is specified about Q and $\dot{Q}$ at some instant of time.

The same reasoning can be applied to the excited state to give

$$E_1 + \tfrac{1}{2}m\dot{Q}^2 + \tfrac{1}{2}k_e(Q - \Delta)^2 + p_a Q = C' , \tag{23}$$

where C' is a constant.

The first three terms on the left of Eqs. (22) and (23) represent the total crystal energy. Equations (22) and (23) show explicitly that it is not conserved in a vibration cycle at constant pressure. The term $p_a Q$ present in both equations represents energy transferred from the crystal to the apparatus which produces the pressure. We show this point explicitly with a model pressure apparatus in Sec. VI. One can rewrite Eq. (22) in a very simple form as

$$\tfrac{1}{2}m\dot{Q}^2 + \tfrac{1}{2}k_g(Q + p_a/k_g)^2 = C + p_a^2/2k_g - E_0 \tag{24}$$

and similarly for the excited state

$$\tfrac{1}{2}m\dot{Q}^2 + \tfrac{1}{2}k_e(Q - \Delta + p_a/k_e)^2 = C' + p_a^2/2k_e - E_1 . \tag{25}$$

One can identify the quantities on the left as kinetic and potential energies, the potential energy being parabolic in form. The Q corresponds to the minimum, displaced by $-p_a/k_g$ or $-p_a/k_e$ for ground and excited states, from its value in the absence of pressure.

We must note, however, that Eq. (21) clearly shows this potential energy is not the potential energy of the crystal alone, but also includes energy the crystal supplies to the pressure apparatus during the displacement of Q under pressure.

Both C and C' can be determined if initial conditions of Q and $\dot{Q}$ are given. In the most general case, C and C' can be picked independently. However, if C is picked for the ground state and an optical excitation is made, since Q and $\dot{Q}$ do not change during the excitation, C' can be determined in terms of C. In fact, as we have discussed, the optical quantum must supply the difference in total crystal energy so that

$$E_0 + \tfrac{1}{2}m\dot{Q}^2 + \tfrac{1}{2}k_g Q^2 + h\nu = E_1 + \tfrac{1}{2}m\dot{Q}^2$$
$$+ \tfrac{1}{2}k_e(Q - \Delta)^2 . \tag{26}$$

Whence

$$C' = C + h\nu . \tag{27}$$

IV. METHOD OF CURIE, BERRY, AND WILLIAMS

A. Comparison of the CBW and DFS expressions

Curie, Berry, and Williams calculate a quantity they call $E_\alpha(p,R)$ (where α is labeled g or e for the

ground and excited states). $E_\alpha(p,R)$, which depends on p and the generalized coordinate R (using their notation) has the units of energy. They treat $E_\alpha(p,R)$ like a potential energy to draw a configuration coordinate diagram. They then state that the optical transition occurs at frequency $\nu(p)$ given by

$$h\nu(p) = E_e(p,R) - E_g(p,R) \ , \tag{28}$$

where $E_e(p,R)$ and $E_g(p,R)$ are calculated for the equilibrium value of R in the ground state under pressure. Whether or not Eq. (28) is true of course depends on the definition of $E_\alpha(p,R)$. As we explain, we do not believe Eq. (28) is true for their definition.

$E_\alpha(p,R)$ is calculated by a method we describe below. They find [Eq. (2) in their paper]

$$E_\alpha(p,R) = E_\alpha(0) + \tfrac{1}{2}k_\alpha[R - R_\alpha(p)]^2 + p^2/2k_\alpha \ , \tag{29}$$

where in the DFS notation

$$R = Q \ .$$

$R_g(0)$ and $R_e(0)$ are the equilibrium values of R at zero pressure for the ground and excited states, respectively, so that

$$R_g(0) = 0 \ , \tag{30a}$$

$$R_e(0) - R_g(0) = \Delta \ , \tag{30b}$$

$$E_g(0) = E_0 \ , \tag{30c}$$

$$E_e(0) = E_1 \ , \tag{30d}$$

and

$$R_\alpha(p) - R_\alpha(0) = -p/k_\alpha \ . \tag{31}$$

As we discuss below, given their prescription for calculating $E_e(p,R)$ we agree with their specific result Eq. (29). However, we do *not* agree that this quantity is appropriate for use in Eq. (28).

We now use Eq. (31) to transform Eq. (29) into two alternate forms. We give the complete algebraic details so the reader can verify that we have done the calculation correctly. First we transform the second term on the right

$$E_\alpha(p,R) = E_\alpha(0) + \tfrac{1}{2}k_\alpha[R - R_\alpha(0) + R_\alpha(0) - R_\alpha(p)]^2 + p^2/2k_\alpha \tag{32a}$$

$$= E_\alpha(0) + \tfrac{1}{2}k_\alpha[R - R_\alpha(0)]^2 + k_\alpha[R - R_\alpha(0)][R_\alpha(0) - R_\alpha(p)] + \tfrac{1}{2}k_\alpha[R_\alpha(0) - R_\alpha(p)]^2 + p^2/2k_\alpha \ . \tag{32b}$$

Using Eq. (31) and the third term we get

$$E_\alpha(p,R) = E_\alpha(0) + \tfrac{1}{2}k_\alpha[R - R_\alpha(0)]^2 + p[R - R_\alpha(0)]$$
$$+ \tfrac{1}{2}k_\alpha[R_\alpha(0) - R_\alpha(p)]^2 + p^2/2k_\alpha \ . \tag{32c}$$

Using Eq. (31) we transform the fourth term on the right:

$$E_\alpha(p,R) = E_\alpha(0) + \tfrac{1}{2}k_\alpha[R - R_\alpha(0)]^2 + p[R - R_\alpha(0)]$$
$$+ \tfrac{1}{2}k_\alpha\left(\frac{-p}{k_\alpha}\right)^2 + \frac{p^2}{2k_\alpha} \ , \tag{32d}$$

$$E_\alpha(p,R) = E_\alpha(0) + \tfrac{1}{2}k_\alpha[R - R_\alpha(0)]^2$$
$$+ p[R - R_\alpha(0)] + p^2/k_\alpha \ . \tag{33}$$

Equation (33) is a useful form of displaying the result of CBW. All the pressure dependence is explicit. Another useful form for their result is found by again using Eq. (31) to transform p^2/k_α

$$p^2/k_\alpha = p[R_\alpha(0) - R_\alpha(p)] \tag{34}$$

giving

$$E_\alpha(p,R) = E_\alpha(0) + \tfrac{1}{2}k_\alpha[R - R_\alpha(0)]^2$$
$$+ p[R - R_\alpha(0) + R_\alpha(0) - R(p)] \tag{35a}$$

or

$$E_\alpha(p,R) = E_\alpha(0) + \tfrac{1}{2}k_\alpha[R - R_\alpha(0)]^2 + p[R - R_\alpha(p)] \tag{35b}$$

We now can compute the CBW expression for the optical absorption by means of Eq. (28) and either Eq. (33) or (35b) recognizing, as CBW do, that for R we use the equilibrium value in the ground state

$$R = R_g(0) - (p/k_g) = R_g(p) \ . \tag{36}$$

Delaying this substitution, we get from Eq. (33)

$$h\nu(p) = E_e(0) - E_g(0)$$
$$+ \tfrac{1}{2}k_e[R - R_e(0)]^2 - \tfrac{1}{2}k_g[R - R_g(0)]^2$$
$$+ p[R_g(0) - R_e(0)] + (p^2/k_e) - (p^2/k_g) \ , \tag{37}$$

or from Eq. (35b)

$$h\nu(p) = E_e(0) - E_g(0)$$
$$+ \tfrac{1}{2}k_e[R - R_e(0)]^2 - \tfrac{1}{2}k_g[R - R_g(0)]^2$$
$$+ p[R_g(p) - R_e(p)] \ . \tag{38}$$

Comparing either Eq. (37) or (38) with the DFS expression Eq. (15b) [using Eq. (30) to relate the notation] we see that the terms in the first and second lines of Eq. (37) or (38) agree with Eq. (15b) but that CBW have an extra term which is the third line of each equation. We contend that the term in the third line implies that in going from the ground to the excited state the light quantum must not only supply the crystal electronic energy difference and the crystal elastic energy difference, but also does work against pressure in the amount

$$\text{Work} = -p\Delta + p^2\left(\frac{1}{k_e} - \frac{1}{k_g}\right) . \tag{39}$$

Since in the optical transition R (or Q) does not change, there should be no work against pressure. *We argue that the CBW expression must be in error since their result implies work is done against pressure in a process in which the volume does not change.*

As we explain below in detail, the energies used by CBW include not only the total crystal energy, but *also* a work term done by the crystal against the pressure apparatus defined in such a manner that, at the same Q, it is different in the ground and excited states.

B. CBW's method

CBW's definition of $E_\alpha(p,R)$ is the sum of three terms, $E_\alpha(0)$ and two quantities with the units of energy which they call W_1 and W,

$$E_\alpha(p,R) = E_\alpha(0) + W_1 + W . \tag{40}$$

CBW first calculate W_1, and then in a second step calculate W. We shall use their two steps, but use the concepts (1), (2), (3), or (4) of crystal elastic energy to evaluate W_1 and W. While our procedure and results agree with theirs for both W_1 and W, our method of calculation emphasizes the distinction between energy which resides in the crystal and energy which resides in the pressure apparatus. According to the Franck-Condon principle, only the former changes during the actual optical transition.

CBW consider the system to be initially in equilibrium in state $\alpha(\alpha = g$ or $e)$ under zero pressure. That is, $R = R_\alpha(0)$, and the crystal energy is $E_\alpha(0)$. In step one, the pressure is slowly increased to its value p, changing R to $R_\alpha(p)$, its equilibrium value at pressure p. W_1 is defined as the work done on the crystal by the applied pressure as the pressure is built up from its initial value to its final value p. Since this work goes into the crystalline elastic energy we may write [as in Eq. (3)]

$$W_1 = \frac{1}{2}k_\alpha[R_\alpha(p) - R_\alpha(0)]^2 . \tag{41}$$

Once the pressure has been applied, the system is in equilibrium at $R_\alpha(p)$. However, the system could be displaced from this value by application of an additional force F. If it were displaced by such a force and the force were suddenly removed, R would oscillate harmonically about the equilibrium $R = R_\alpha(p)$. To describe such a circumstance, CBW define a potential energy $W(R)$. They calculate $W(R)$ by considering how R varies as F is built up from zero. By building up F slowly, (the adiabatic approximation), negligible kinetic energy is given the system, so that $W(R)$ is simply the work done by F in displacing R from $R_\alpha(p)$ to R. This definition of $W(R)$ makes $W(R_\alpha(p)) = 0$.

We now calculate $W(R)$. We do it in an alternate manner to that of CBW, but obtain the same result as they do.

Since F is the force which would hold the crystal in equilibrium at coordinate R, it must just balance the sum of the elastic restoring force and the applied pressure. CBW define F to be positive inwards so that

$$F = -k_\alpha[R - R_\alpha(0)] - p . \tag{42}$$

To calculate W we note that F must do two things as R goes from $R_\alpha(p)$ to R:

(i) Supply the change in crystalline elastic energy

$$\frac{1}{2}k_\alpha[R - R_\alpha(0)]^2 - \frac{1}{2}k_\alpha[R_\alpha(p) - R_\alpha(0)]^2$$

(ii) Supply work the crystal does against the constant pressure. Since this is just the negative of the work the pressure does on the crystal, and since the pressure is constant, this work is just $p[R - R_\alpha(p)]$. Therefore

$$W = \frac{1}{2}k_\alpha[R - R_\alpha(0)]^2 - \frac{1}{2}k_\alpha[R_\alpha(p) - R_\alpha(0)]^2$$
$$+ p[R - R_\alpha(p)] . \tag{43}$$

Therefore adding Eqs. (41) and (43) we get

$$E_\alpha(p,R) = E_\alpha(0) + W_1 + W$$
$$= E_\alpha(0) \quad (\text{term A})$$
$$+ \frac{1}{2}k_\alpha[R - R_\alpha(0)]^2 \quad (\text{term B})$$
$$+ p[R - R_\alpha(p)] \quad (\text{term C}) . \tag{44}$$

As we see Eq. (44) agrees with the CBW result given by Eq. (35b). To understand what we have calculated, we examine the significance of terms in the second, third, and fourth lines of Eq. (44).

The term in the second line (term A) is the energy of the crystal when it is in equilibrium at $R = R_\alpha(0)$ prior to application of the pressure. We call this condition the initial state of the crystal.

The term in the third line (term B) is the increase in the crystalline elastic potential energy from its

value in the initial state for which $R = R_\alpha(0)$, to the value at R. It is therefore the work one must do against the elastic forces in displacing R from $R_\alpha(0)$ to R.

The sum of terms A and B clearly gives the total crystal energy at coordinate R.

The term in the fourth line (term C) is the work the crystal does on the pressure producing system during the displacement from $R = R_\alpha(p)$, the equilibrium position in state α under action of the pressure, to the final value of R. The extra term C represents energy which does not reside in the crystal, but rather has been transferred from the crystal to the pressure apparatus during the displacement of R from $R_\alpha(p)$ to R. A similar situation was discussed in connection with the derivation of Eq. (21b).

As long as one is not considering optical transitions $E_\alpha(p,R)$ may be considered as an effective potential energy for describing the behavior of R at fixed p. Thus, free vibrations of R about the equilibrium at fixed p obey the equation

$$\tfrac{1}{2}m\dot{R}^2 + E_\alpha(p,R) = \text{const} . \tag{45}$$

However, $E_\alpha(p,R)$ has built into it a convention that the work the crystal does against pressure when R changes is measured from *a standard state* $[R = R_\alpha(p)]$ which is *different for different* α. Therefore, even though R does not change in an optical transition so that in fact there is no work done against pressure during the optical transition, term C contributes to Eq. (28) simply because the standard state changes. *As we demonstrate in the next two sections for optical transitions, the same standard state must be chosen for term C for both electronic states in order to avoid a spurious work-against-pressure contribution to the calculations of the energy of the light quantum.*

Alternatively, one can simply recognize that terms A and B by themselves give the total energy of the crystal once the state α is specified and the coordinate R is selected. Then, since the crystal does no work against pressure during the optical transition, the entire energy of the light quantum must go into the changing terms A + B at fixed R. This procedure is what DFS use, as outlined in Sec. II.

V. ANALYSIS OF A CONCRETE EXAMPLE — QUALITATIVE EXPLANATION

The entire disagreement between DFS and CBW arises because of term C in Eq. (44) and quite specifically because CBW measure the work the crystal does against the pressure apparatus from different values of R for the ground and excited states. The proper choice of standard states as well as further insight into the energy transfers can be seen by considering a model which gives an explicit description of a pressure apparatus. In this model we see that the method of CBW *necessarily* assumes that the pressure apparatus has a configuration change during the optical transition, a circumstance we believe violates the Franck-Condon principle.

Accordingly considering Fig. 1 we show a pressure vessel containing a sample (volume V_0) immersed in an incompressible fluid. Pressure can be applied to the fluid by a piston which slides without friction in a tube of cross-sectional area A. A spring of unstretched length L and spring constant k_0 is attached at one end to the piston (coordinate X) and at the other end (coordinate Y) to an external force of magnitude F_{ext} (taken as positive to the left, so that a positive F produces compression).

In a typical experiment, F_{ext} is built up slowly (to avoid kinetic energy) pushing in the piston, and exerting a pressure $p = F_{ext}/A$. In the process of building up the pressure, the piston moves to the left, as does the point of application of F_{ext}. During the buildup of pressure, F_{ext} does work which goes into compression of the sample (crystal elastic potential energy) and compression of the spring (spring elastic potential energy).

Once the pressure has been built to the desired value, we clamp the right-hand end of the spring to assure that no more work can be done by F_{ext} on the system of spring, sample, and pressure vessel. That is, we hold Y fixed.

Figure 2 shows the apparatus at zero pressure for two different electronic states. In Fig. 2(a) the sample is in the ground electronic state and has volume V_0. We define the piston position in this case as $X = 0$. Accordingly $Y = L$.

Figure 2(b) corresponds to the sample being *in equilibrium* at zero pressure in the excited electronic state with volume V_1. The fact that $V_1 \neq V_0$ requires now that $X \neq 0$ for this case. In fact

$$X = (V_1 - V_0)/A \tag{46a}$$

and

$$Y = [(V_1 - V_0)/A] + L . \tag{46b}$$

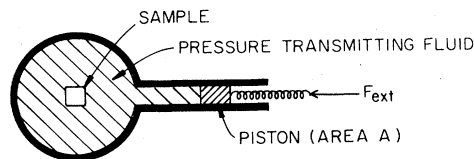*We note that at zero pressure, the state of the pressure*

FIG. 1. Schematic diagram of a sample contained in a pressure bomb. Pressure is applied by an external force, F_{ext}, acting on a frictionless piston, and is transmitted to the sample by means of an incompressible pressure transmitting fluid.
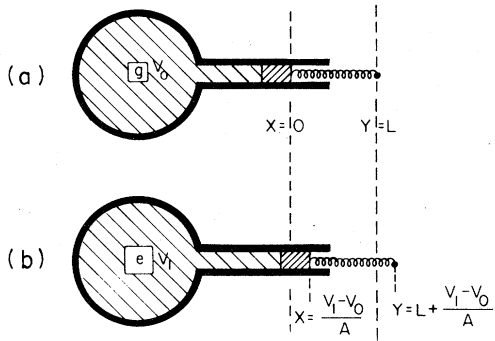
FIG. 2. The pressure apparatus of Fig. 1 for two states of the sample both corresponding to zero pressure. The spring has uncompressed length L, its left-hand end at coordinate X, and its right-hand end at coordinate Y. (a) With the pressure set to zero when the sample is in its ground electronic state, g, the corresponding volume is V_0 and X is defined as 0. Thus $Y = L$. Figure 2(a) corresponds to the zero pressure configuration of both DFS and CBW when the system is in the ground electronic state. (b) When the pressure is set to zero with the sample in its excited electronic state, e, the sample volume is V_1, so the piston must be $(V_1 - V_0)/A$ to the right of its position in Fig. 2(a), hence $X = (V_1 - V_0)/A$ and $Y = L + (V_1 - V_0)/A$. Figure 2(b) corresponds to the zero configuration used by CBW for the case where the pressure is set to zero with the system in the excited electronic state.

apparatus is different in these two cases. In particular, the value of Y differs.

If the system of Fig. 2(a) (ground state at zero pressure) were excited optically, the circumstances immediately after excitation would be those of Fig. 3(a). The sample volume would still be V_0, immediately after excitation into state e. Eventually the excited state would settle down to volume V_1, and the situation would be as in Fig. 3(b). Note, however, that Fig. 2(b) and Fig. 3(b) differ. Similar figures could be drawn for the case of an applied pressure. Figure 2(b) corresponds to the CBW approach of starting first in the excited state, then applying pressure. Figure 3(b) corresponds to applying pressure in the ground state.

In Fig. 3(c) we see Y corresponding to the case of zero pressure applied in the excited state, the sample in the excited state, but with volume V_0 of the ground state. Figure 3(c) corresponds to the CBW formulas for the energy of the excited state produced by optical excitation. *Contrasting Figs. 3(a) and 3(c) we note that the optical transition does not go to the CBW state.*

Another way of expressing matters is that specifying the state of the pressure apparatus requires specifying the coordinate Y as well as the sample volume (which specifies X). In an optical transition *neither* Y nor X change. The procedure used by CBW has the effect of keeping X fixed, but *changing* Y during the
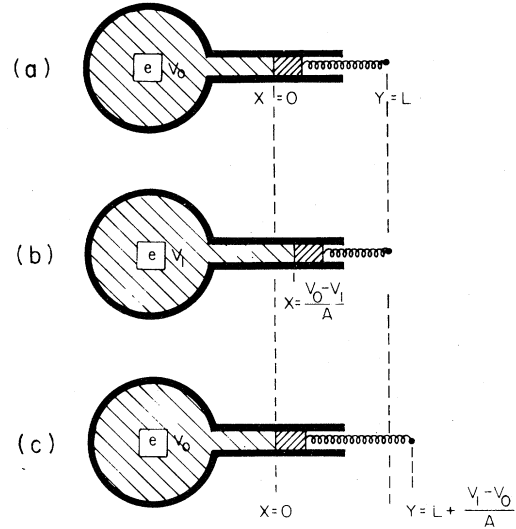

FIG. 3. The pressure apparatus for three states of the system, all at zero pressure. (a) The situation immediately following optical excitation from state g to e. Since, prior to optical excitation, the system was at equilibrium under zero pressure in state g, X and Y are identical to their situation in Fig. 2(a). Since the lattice atoms do not move during the optical transition, the sample volume is V_0, its value in the ground state just prior to excitation. This figure corresponds to the excited-state configuration DFS calculate. (b) The situation of Fig. 3(a) puts the lattice vibrations in a highly excited state. If these vibrations die down while the lattice remains in the excited electronic state, the system arrives at the configuration Fig. 3(b), with the sample in equilibrium in state e at volume V_1. Note that although the *sample* is in the same state as Fig. 2(b), the coordinate Y is different because the pressure apparatus was adjusted to produce zero pressure when the sample was in the ground state. (c) The configuration immediately after optical excitation from the ground state according to the CBW calculation. The Y coordinate corresponds to the pressure apparatus being adjusted to zero pressure with the sample in the excited state [Fig. 2(b)], but the volume of the sample is V_0 corresponding to the ground state. Note that while $X = 0$ as in the DFS configuration [Fig. 3(a)], Y differs from its value in Fig. 3(a).

optical transition. That they change Y is the result of their definition of the energy $E_\alpha(p,R)$ which they use to calculate the optical frequency.

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We now proceed to work out the details of the various configurations of Figs. 2 and 3. The problem can be treated by replacing the details of the pressure vessel with an equivalent system shown in Fig. 4, which is a linear arrangement of two springs, one representing the crystalline elastic potential energy, the other representing the elastic potential energy
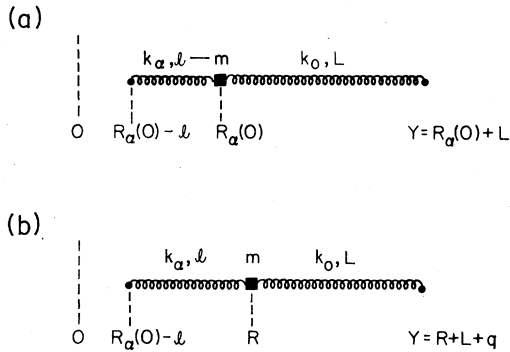
(a)

(b)

FIG. 4. Schematic representation of sample and pressure apparatus for state α (where $\alpha = g$ or e for ground or excited electronic states). (a) The situation at zero pressure. The sample is represented by a spring of unstretched length l, spring constant k_α, and mass m. The pressure is applied by a spring of unstretched length L, and spring constant k_0. $R_\alpha(0)$ is the coordinate of m at zero pressure. (b) The general situation. The mass is now at position R, the pressure spring has an extension q, so that the right-hand end of the pressure spring is at coordinate $Y = R + L + q$. To apply pressure adiabatically, Y is slowly moved to the left from its value $[R_\alpha(0) + L]$ of Fig. 4(a). Once pressure is applied, Y is held fixed. If the mass is in equilibrium R is at $R_\alpha(p_a)$. However, more generally R is not in equilibrium, as, for example, immediately following an optical excitation.

of the pressure apparatus. We label this the "pressure spring." The linear arrangement will enable us to keep track of energy, and to see in quantitative detail why DFS and CBW differ.

For this system the following general relationships hold. If we define the variable q as the amount the pressure spring is stretched (so that negative values of q corresponds to compression)

$$Y = R + L + q \ . \tag{47}$$

The pressure, p, exerted by the pressure spring on the crystal is

$$p = -k_0 q \ . \tag{48}$$

(Note that we assume unit areas so that forces and pressures are equivalent.) The crystal potential energy, U_c, is $E_\alpha(0) + \frac{1}{2}k_\alpha[R - R_\alpha(0)]^2$. The pressure spring potential energy, U_p, is $\frac{1}{2}k_0 q^2$.

Therefore, the total potential energy of the system of pressure spring plus crystal in state α, $U_{tot}(\alpha)$, is the sum of these two terms:

$$U_{tot}(\alpha) = E_\alpha(0) + \frac{1}{2}k_\alpha[R - R_\alpha(0)]^2 + \frac{1}{2}k_0 q^2 \ . \tag{49}$$

Denoting the total energy of the system of crystal plus pressure spring as $W_{tot}(\alpha)$, we have for the sys-

tem in state α

$$W_{tot}^{(\alpha)} = \frac{1}{2}m\dot{R}^2 + U_{tot}(\alpha)$$

$$= \frac{1}{2}m\dot{R}^2 + E_\alpha(0) + \frac{1}{2}k_\alpha[R - R_\alpha(0)]^2 + \frac{1}{2}k_0 q^2 \ . \tag{50}$$

We now note several ways of writing $U_{tot}(\alpha)$. In the first one, we utilize Eq. (47) to express q. This gives us

$$U_{tot}(\alpha) = E_\alpha(0) + \frac{1}{2}k_\alpha[R - R_\alpha(0)]^2 + \frac{1}{2}k_0(Y - R - L)^2 \ . \tag{51}$$

We note that there are in this expression *two* independent variables, R and Y. *Specification of the state of the system requires specification of both R and Y.* The value of Y, which designates the right-hand coordinate of the pressure spring, is determined by two things: (1) the pressure applied to the system; and (2) the state of the system in which the pressure is applied.

Equation (51) is especially useful for computing the optical transition frequencies. Application of the principle that *neither R nor Y can change in the transition*, together with assumption that $\dot{R} = 0$, shows immediately from Eq. (47) that the energy of the light quantum is

$$h\nu = U_{tot}(e) - U_{tot}(g) \ , \tag{52a}$$

$$= E_e(0) - E_g(0) + \frac{1}{2}k_e[R - R_e(0)]^2 - \frac{1}{2}k_g[R - R_g(0)]^2 \ , \tag{52b}$$

where R is the equilibrium value in the ground state under the applied pressure. *Equation (52b) is just the DFS result of Eq. (15a).*

Denoting q_a as the value of q when the entire system is at equilibrium in state β at pressure p_a we can use Eqs. (47) and (48) to show that

$$p_a = -k_0 q_a \ , \tag{53}$$

$$Y = R_\beta(p_a) + L - p_a/k_0 \ . \tag{54}$$

Since

$$R_\beta(p_a) = R_\beta(0) - p_a/k_\beta \tag{55}$$

we get

$$Y = R_\beta(0) - p_a/k_\beta - p_a/k_0 + L \ . \tag{56}$$

Therefore, determination of Y depends not only on knowledge of the applied pressure, p_a, but also on specification of the state, β, the system is in when the pressure is applied. These differences are illustrated, of course, by the differences between Fig. 2(a) and Fig. 2(b).

Equation (51) shows that we can plot $U_{tot}(\alpha, R, Y)$ as a function of R for fixed Y. Taking successive

values of Y gives a family of curves, as illustrated in Fig. 5. Since in an optical transition neither R nor Y changes, an optical transition is shown as a vertical arrow. This is the transition DFS use.

The prescription of CBW calculates the ground-state energy by applying the pressure to the system when in the ground electronic state, and calculates the excited-state energy by applying the pressure to the system when in its excited electronic state. It therefore picks out ground and excited states of different Y. Specifically, their prescription leads to

$$Y_g = R_g(0) - p_a/k_g - p_a/k_0 + L \quad , \tag{57a}$$

$$Y_e = R_e(0) - p_a/k_e - p_a/k_0 + L \quad , \tag{57b}$$

so

$$Y_e - Y_g = R_e(0) - R_g(0) + p_a \left(\frac{1}{k_g} - \frac{1}{k_e} \right) \quad . \tag{57c}$$

So, although their transition is in a plane of constant R, it is not in a plane of constant Y. Such a transition is shown also in Fig. 5. The Franck-Condon principle
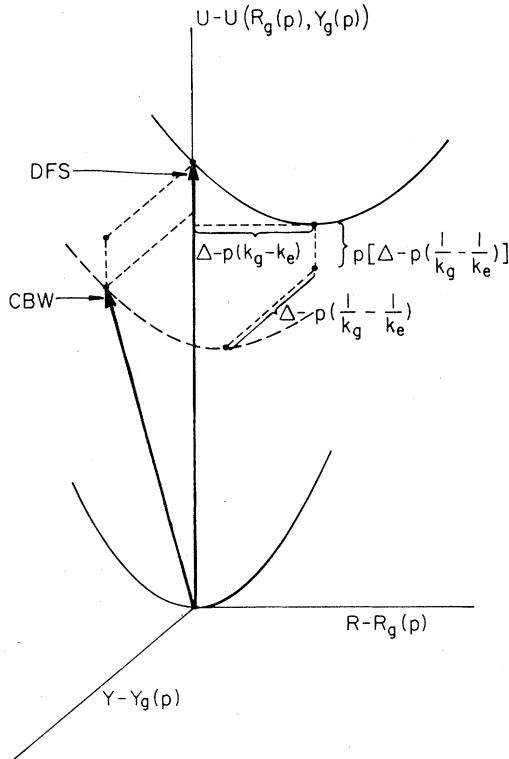

FIG. 5. Transitions according to CBW and DFS. DFS keep both the pressure apparatus (Y) and the harmonic-oscillator coordinate (R) fixed during the transition in accordance with the Franck-Condon principle. The technique of calculation employed by CBW causes (Y) to change [see Eqs. (57a) and (57b)].

requires that neither R nor Y change. The DFS prescription is to use the values of both R and Y found for the ground state to calculate U_{tot} for both ground and excited states.

These considerations can be followed in detail to show that they account quantitatively for the different expressions of DFS and CBW. To do so, it is convenient to reexpress the pressure spring elastic energy. Suppose we designate the value of q corresponding to equilibrium at pressure p_a as $q(p_a)$. If the system were in state β, the equilibrium value of R would be $R_\beta(p_a)$. Then if the system is in state β, but $R \neq R_\beta(p_a)$ (i.e., the system is not in equilibrium), we have

$$q = q(p_a) + R - R_\beta(p_a) \quad . \tag{58}$$

We can utilize Eq. (58) to express the pressure spring elastic energy, U_p,

$$U_p = \frac{1}{2} k_0 q^2 \tag{59a}$$

$$= \frac{1}{2} k_0 q_a^2 + k_0 q_a [R - R_\beta(p_a)] + \frac{1}{2} k_0 [R - R_\beta(p_a)]^2 \tag{59b}$$

In order to guarantee that the pressure does not vary as R varies (at fixed Y) we want $[q - q(p_a)]/q(p_a) \ll 1$. This can be achieved if $k_0 \ll k_\alpha$. We assume this condition satisfied. Then we can neglect the third term of Eq. (59b) with respect to the first two. Utilizing Eq. (48) we can eliminate q_a in terms of p_a to get

$$U_p = (p_a^2/2k_0) - p_a[R - R_\beta(p_a)] \quad . \tag{60}$$

We see now that in expressing the total potential energy of crystal plus pressure spring we must specify two quantities α and β to specify state of the system. We, therefore, write U_{tot} as $U_{tot}(\alpha, \beta)$ not just $U_{tot}(\alpha)$. If the system is in state α, but the pressure is thought of as having been established in state β, we get

$$U_{tot}(\alpha, \beta) = E_\alpha(0) + \frac{1}{2} k_\alpha [R - R_\alpha(0)]^2$$

$$+ p_a^2/2k_0 - p_a[R - R_\beta(p_a)] \quad . \tag{61}$$

The last two terms, having originated from Eq. (55), represent energy residing in the pressure spring. The first of them is the energy when the spring length is $q_a(p_a)$. The second of them represents the change in the pressure spring energy produced by changing the left-hand end of the pressure spring from $R_\beta(p_a)$ to R. We note in Eq. (61) that for a given α we get different U_{tot}'s depending on whether β is the same or different from α.

We can utilize Eq. (61) to express the conservation

of energy for vibrations of the system in state α:

$$\frac{1}{2}m\dot{R}^2 + E_\alpha(0) + \frac{1}{2}k_\alpha[R - R_\alpha(0)]^2$$

$$-p_a[R - R_\beta(p_a)] + p_a^2/2k_0 = B \quad , \qquad (62)$$

where B is a constant determined once R and $\dot{R}$ are known for a given p_a and $R_\beta(p_a)$. Equation (62) contains *both* the result of DFS [Eqs. (22) and (23)] and the result of CBW [Eqs. (35) plus (45)]

$$\frac{1}{2}m\dot{R}^2 + E_\alpha(0) + \frac{1}{2}k_\alpha[R - R_\alpha(0)]^2$$

$$+ p_a[R - R_\alpha(p_a)] = \text{const} \qquad (63)$$

at constant p_a.

Taking $\dot{R} = 0$ in the ground and excited states we see that the DFS expression for the frequency of the optical transition [Eq. (15)] represents the equation

$$h\nu(R) = U_{\text{tot}}(e,g) - U_{\text{tot}}(g,g) \quad , \qquad (64)$$

whereas the CBW expressions [Eqs. (24) and (31b)] is

$$h\nu(R) = U_{\text{tot}}(e,e) - U_{\text{tot}}(g,g) \quad . \qquad (65)$$

Clearly Eq. (64) is the correct expression to use since the system when found in the excited state had its pressure established in the ground state. Specifically, the CBW expression, Eq. (65) corresponds, according to Eqs. (57a) and (57b) to different values Y in the ground and excited states, hence violates the Franck-Condon principle.

Substitution of explicit expressions for the U_{tot} from Eq. (61) into Eqs. (64) and (65) gives us

$$h\nu(R)_{\text{DFS}} = E_e(0) - E_g(0) + \frac{1}{2}k_e[R - R_e(0)]^2$$

$$- \frac{1}{2}k_g[R - R_g(0)]^2 \quad , \qquad (66)$$

which is the DFS result Eq. (15a) and

$$h\nu(R)_{\text{CBW}} = E_e(0) - E_g(0) + \frac{1}{2}k_e[R - R_e(0)]^2$$

$$- \frac{1}{2}k_g[R - R_g(0)]^2$$

$$+ p_a[R_e(p_a) - R_g(p_a)] \quad . \qquad (67)$$

Recognizing that $R_\alpha(p_a) = R_\alpha(0) - p_a/k$ we see that Eq. (67) is the CBW result.

Thus, our example shows that we have been able to reproduce both the results of DFS and CBW with the concrete model. *The model shows that CBW violate the Franck-Condon principle because their method of calculation implies a change in the pressure apparatus during the optical transition.*

ACKNOWLEDGMENTS

APPENDIX: THE EXPERIMENTAL SITUATION

The justification of an analysis must lie primarily in its consistency and correctness. Since, however, Curie *et al.*, have mentioned possible experiments apparently consistent with their analysis, it seems desirable to bring to the reader's attention a few experimental observations.

(1) For a large number of aromatic hydrocarbons in liquid solution, in plastic films, and in the crystalline state, shifts to lower energy with increasing pressure are observed for both absorption and fluorescence[6,7] in contradiction to the CBW analysis. Similar observations have been made on heterocyclic molecules. A single configuration coordinate model should apply to these materials. However, where the bulk modulus changes strongly with pressure, as in organic crystals and polymers, a strictly harmonic analysis can be applied *quantitatively* only under some serious approximations.

(2) The Mn^{+2} ion in a variety of environments[8,9] gives an emission which shifts to lower energy with increasing pressure. The absorption also shifts to lower energy with pressure where it can be observed.[10,11] This is to be expected, as, for this d^5 system, the energy difference between ground and excited states does not involve the ligand field strength Dq but only the interelectronic repulsion parameters (Racah parameters) which have been shown always to decrease with increasing pressure.[11] Again, a single configuration coordinate analysis should apply.

(3) The heavy-metal ion in alkali halides which CBW use is not a valid system for applying the same configuration coordinate to both absorption and emission. The excited state is Jahn-Teller (JT) split[12-15] and the emission is from one or the other (or both) of the JT states, not necessarily the state to which the electron is excited. Incidentally, the CBW analysis predicts that the half width for absorption and emission should change in the same direction with pressure, while, for the heavy metals in alkali halides, the absorption half width *increases* significantly while the emission peak *narrows* dramatically as pressure increases.

A number of other examples could be cited which are hard to reconcile with the CBW analysis. For example, there are many emission-peak shifts which are linear with pressure over a range of 100–200 kbar; e.g., ruby,[16] $BaSiO_5$:Pb (Ref. 12), $Ca_3(PO_3)_2$:Sb:Mn (manganese emission) (Ref. 10) $Zn_3(PO_4)_2$:Mn, a large group of tungstate and molybdate phosphors,[17] and a series of phosphates, silicates, and aluminates doped with Eu^{+2}.[18]

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