Analysis of the effects of high pressure on the spectra of molecular crystals

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The failure of the Drickamer, Frank, and Slichter (DFS) theory, as modified by Okamoto and Drickamer to fit the experimental data on the pressure-dependent spectra of aromatic materials is analyzed quite generally. Possible explanations are (a) different coordinates are important for the optical and pressure effects, (b) anharmonicity is improperly included in the modified theory, and (c) the omission of the direct effect of pressure on the adiabatic potential is responsible. We show, in the analysis of (a), that a many-coordinate harmonic system can be reduced to a one-coordinate model with pressure-dependent force constants and, in the analysis of (c), that the data on the aromatic compounds cannot differentiate between the modified DFS theory and a similarly modified Curie, Berry, and Williams (CBW) theory, which includes the direct effect of pressure on the adiabatic potentials. Therefore, we conclude that (b) is responsible for the failure, verifying Tompkins' earlier conclusion. We have also generalized his consistency tests and clarified the type of data needed to test the respective validities of the DFS and of the CBW theories.

I. INTRODUCTION

One of us (RCT) has published a critical analysis[1] (hereafter referred to as T) of the effect of hydrostatic pressure on the electronic spectra using the model of Drickamer, Frank, and Slichter[2,3] (DFS) as modified by Okamoto, Drotning, and Drickamer[4] (ODD) to the data of Okamoto and Drickamer[5] (OD). T concluded that "the tests fail to verify the model, even qualitatively." He then applied the multicoordinate model of Lin,[6] obtaining qualitative consistency, and suggested that the quantitative agreement might be improved by including anharmonicity. Such an extension of the model has been carried out in terms of a Morse potential,[7] but evaluation in terms of experimental data has not been feasible. Note that the Lin model as a single configurational coordinate model is basically equivalent to the DFS model in the harmonic case except for the coupling constant, as noted by Lin.

We note that basic problems exist in the DFS theory and that another theory has been proposed by Curie, Berry, and Williams[8–11] (CBW) in which the direct effect of the pressure on the radiative transition energy is included. This effect was anticipated by Alers and Dolecek[12] and, in part, by Johnson and Williams.[13] For an analysis of both points of view, i.e., the DFS and CBW theories, see Refs. 14 and 15. The CBW theory assumes a coupled system involving the impurity subsystem and the pressure apparatus, for which generalized adiabatic curves are pressure dependent. The important consequences for optical spectra are (a) the adiabatic potentials are pressure dependent, and (b) the pressure effects are, in general, different for each electronic state, so that the transition energy at a given configuration is pressure dependent. From the pressure dependent adiabatic potentials and a generalized Franck–Condon (FC) principle,[15] we can determine the optical spectra. This generalized FC principle, in addition to the usual conditions of having the configuration and momentum constant during an optical transition, includes the condition that the pressure on the system must be constant. The spectra are then found in the usual way from these configurational curves plus this FC principle.

The purpose of this paper is to re-examine the consistency tests of T. We find that some changes must be made in the analysis. Applying the resulting tests to the OD data, we find the same results previously reported by T. We also develop some general tests which must be satisfied by the data so that either the modified DFS theory or a similarly modified harmonic form of the CBW theory is applicable to the data. In addition, we derive consistency tests between the experimental parameters. We find that the data of OD fail these general tests. We then make some general observations about the applicability of both of these modified theories to the molecular crystals studied by OD and to data for other materials.

II. RE-EXAMINATION AND EXTENSION OF TOMPKINS' ORIGINAL WORK

We note that some changes have to be made in the original Tompkins analysis. He assumed that both roots of his Eq. (3.5), Eq. (1) here, for the peak position of absorption

$$Rq^2\omega^4 - [2a_2 P^2 + 2(a_1 - Rq)P + Rq^2\omega_0^2]\omega^2 + (R-1)P^2 = 0 ,$$

(1)

were equal to those of his Eq. (3.6), Eq. (2) here, for the half-width of absorption

$$R^2 q^2 \omega^4 + [2R(R-1)qP - 2E_a P - D_a P^2$$
$$- R^2 q^2 \omega_0^2] \omega^2 + (R-1)^2 P^2 = 0 , \qquad (2)$$

from which he derived that $R = 1$. (Throughout this paper we use the notation of T, which is summarized in Appendix A.) Using the result that $R = 1$, he was then able to derive the following condition for the experimentally determined parameters e_2 and a_2:

$$a_1 + e_2 = 0 , \qquad (3)$$

which was not met by the data of OD.[5]

However, since the half-width and peak position are independent measurements, we would expect to have only one root of Eq. (1) equal to one root of Eq. (2), from which we see that R is not necessarily equal to one. On the other hand, there are similar conditions which the experimental data must meet in order that they satisfy the modified DFS theory. These new conditions are derived using the equation for the peak position for absorption [Eq. (1)] and its emission analog

$$R^2 q^2 \omega^4 + R[2Re_2 P^2 + 2(Re_1 - q)P$$
$$- Rq^2 \omega_0^2] \omega^2 - (R-1)P^2 = 0 , \qquad (4)$$

together with the less stringent condition that only one root of Eq. (1) be equal to one root of Eq. (4). We find that

$$a_2 + Re_2 = (R^2 - 1)/2R\omega_0^2 , \qquad (5)$$

which reduces to Eq. (3) when $R = 1$. In addition, we find that

$$a_1 + Re_1 = (R+1)q \qquad (6)$$

and

$$R^2 e_1 + E_a = R^2 q . \qquad (7)$$

Details of these derivations are given in Appendix B. It may be noted that Eq. (6) was used directly in the OD analysis appearing in Okamoto's dissertation.[16]

Continuing this type of analysis and using in addition the equations for the half-widths of the emission and absorption, we can derive a series of equalities involving both the experimental and theoretical quantities similar to Eqs. (5)–(7). These equalities are given in Appendix B in Eqs. (47) and (48). In addition, we find that the form of ω^2 is then

$$\omega^2 = \omega_0^2 \left\{ 1 + \frac{2(a_1 - Rq)}{R^2 q^2 \omega_0^2} P + \left[\frac{2a_2 \omega_0^2 - (R-1)}{Rq^2 \omega_0^4} \right] P^2 \right\} . \qquad (8)$$

We note that Eq. (8) is formally identical with the OD hypothesis [Eq. (36)].

Before continuing with the general case, we will derive the results for some special cases. If we postulate that

$$\omega^2 = \omega_0^2 z(P) , \qquad (9)$$

then upon substitution into Eqs. (1) and (4) and eliminating the ω^4 term, we find that

$$z(P) = \frac{(R^2 - 1)P}{2R\omega_0^2 [(Re_2 + a_2)P + (Re_1 + a_1) - (R+1)q]} . \qquad (10)$$

Now, from the definition of $z(P)$, the limit as P goes to zero of $z(P)$ should be one, which implies that Eq. (6) must hold and that

$$z(P) = \frac{R^2 - 1}{2R\omega_0^2(Re_2 + a_2)} = 1 , \qquad (11)$$

which implies that Eq. (5) must hold. We note, then, that z is independent of the pressure. In addition, we find that

$$a_1 = qR , \qquad (12)$$
$$R^2 = a_1/e_1 , \qquad (13)$$

and

$$R^2 = a_2/e_2 , \qquad (14)$$

from which we find

$$\omega^2 = \omega_0^2 = \frac{(R-1)}{2a_2} \qquad (15)$$

and that

$$\omega'^2 = \frac{2a_2 R}{R-1} . \qquad (16)$$

These restricted results apply whenever ω^2 is independent of the pressure, which we will see is the case whenever a material behaves harmonically and only one configurational coordinate is important. Equations (12)–(14) are implicit in Okamoto's Eqs. (52a)–(52d).[16] It is not straightforward to take the limit as R goes to one in the above equations, and therefore we consider the case of $R = 1$.

Now, if $R = 1$, we can use Eqs. (1), (2), and (4) plus the emission analog to Eq. (2) to derive the special results given by T in Eqs. (3.13)–(3.15), i.e., the consistency tests

$$D_a = D_e , \qquad (17)$$
$$E_a = E_e , \qquad (18)$$
$$D_a = 2a_2 , \qquad (19)$$
$$a_1 + e_1 = 2q , \qquad (20)$$
$$e_1 + E_e = q , \qquad (21)$$

and

$$a_2 + e_2 = 0 . \qquad (22)$$

Returning to the general case of the modified DFS theory, Drickamer and Frank[3] have shown that the theoretical constant R can be related to the experimentally measured half-widths for emission and absorption as follows:

$$R^3 = \frac{\delta \epsilon_a^2(P)/N^2}{\delta \epsilon_e^2(P)/N^2} = \frac{2E_a + D_a P}{2E_e + D_e P} . \qquad (23)$$

We have derived this relationship in Appendix B and have also shown that the theoretical quantities q^2, ω_0^2, and R can be related to the experimentally measured half-widths and peak positions for emission and absorption as follows:

TABLE I. Contains the values of R^3, $R^3_{av.}$, and the

$$\text{max. \% change} \equiv \max_i \left| \frac{R^3_i - R^3_{av.}}{R^3_{avi}} \right| \times 100 \ .$$

$R^3 = (\omega'/\omega)^6$; therefore, the negative values in (C) indicate that the modified theory does not apply to this case.

(A)

Materials \ Pressure (kbar)	20	40	60	80	Av.	Max.% change
Anthracene crystal	0.978	0.953	0.939	0.928	0.95	2.9
Anthracene PMMA	0.969	0.973	0.957	0.964	0.97	1.4
Phenanthrene crystal	0.857	0.857	0.843	0.846	0.85	0.8
Phenanthrene PMMA	0.818	0.818	0.844	0.837	0.83	1.7

(B)

Materials \ Pressure (kbar)	2	4	6	8	10	Av.	Max.% change
Anthracene in hexane	1.5	1.0	1.1	1.1	1.2	1.2	25
Phenanthrene in hexane	0.67	1.0	0.88	0.91	0.92	0.88	24

(C)

Materials \ Pressure (kbar)	20	40	60	80	100	120	Av.	Max.% change
NaCl: Tl	0	−0.12	−0.15	−0.2	−0.21	−0.25	−0.16	100%
KBr: Tl	0	0	−0.018	−0.059	−0.087	−0.146	−0.052	181%

$$q^2\omega_0^2(R+1) = \frac{4[\delta\mathcal{E}_a(P) - \delta\mathcal{E}_e(P)]}{\frac{\delta\epsilon_a^2(P)}{\epsilon_a^2(0)} + \frac{\delta\epsilon_e^2(P)}{\epsilon_e^2(0)}} \ . \qquad (24)$$

In order for the modified DFS theory to be applicable to any data, the right-hand sides of Eqs. (23) and (24) must be constants with respect to the pressure. We will designate these two conditions as test I and II. If these tests are met, then we can determine R and $q^2\omega_0^2$ from Eqs. (23) and (24), respectively.

We find for the OD data that test I is satisfied to within the experimental error and that R is approximately unity for all the data. Okamoto and Drickamer found similar values.[5] We note that test I is not a trivial test since not all data can satisfy it. For example, see the data of Drotning and Drickamer[17] for NaCl: Tl and NaBr: Tl. The application of test I to these materials is given in Table I.

Since R is approximately unity for the OD data, we then have the quantitative result that the experimentally determined constants a_2, e_2, D_a, D_e, E_a, and E_e must satisfy Eqs. (17)–(22). We note, as did T, that Eq. (22) is not satisfied.

We now turn to test II. We find that the OD data do not satisfy this test, i.e., that $q^2\omega_0^2(R+1)$ must be a constant. Therefore, either by the Tompkins tests or by test II, we can see that the modified theory of DFS is not applicable to the OD data. For the application of test II to the OD data, see Table II.

In some situations a simpler form of test II can be used which can be stated as follows: We note that the left-hand side of Eq. (24) is positive and therefore, if

$$\frac{\delta\epsilon_a^2(P)}{\epsilon_a^2(0)} + \frac{\delta\epsilon_e^2(P)}{\epsilon_e^2(0)}$$

is positive, then we must have

$$\delta\mathcal{E}_a(P) > \delta\mathcal{E}_e(P) \ .$$

This simplified test (test IIa) is not met for anthracene neat crystals above 174 kbar, for anthracene in PMMA above 90 kbar, and for tetracene crystals above 66 kbar for the data of OD.

Tests I and II must be satisfied if the modified DFS theory is to be applicable. If tests I and II are satisfied, then, in addition, the data must satisfy eight consistency tests for the DFS theory in order for it to be correct. Consistency test CT I DFS is given by Eq.

TABLE II. Contains the values of $q^2 \omega_0^2 (R+1)$ in units of cm^{-1} and the

$$\text{max.\% change} = \max_i \left| \frac{[q^2 \omega_0^2 (R+1)]_i - [q^2 \omega_0^2 (R+1)]_{av.}}{[q^2 \omega_0^2 (R+1)]_{av}} \right| \times 100.$$

(A)

Materials \ Pressure (kbar)	20	40	60	80	Ave.	Max.% change
Anthracene crystal	1449	1054	759	546	952	52%
Anthracene PMMA	127	84	40	12	66	92%
Phenanthrene crystal	301	242	213	188	236	28%
Phenanthrene PMMA	350	472	610	705	534	34%

(B)

Materials \ Pressure (kbar)	2	4	6	8	10	Av.	Max.% change
Anthracene in hexane	344	363	348	370	420	369	14%
Phenanthrene in hexane	245	172	191	212	219	208	18%

(5), CT II DFS by Eq. (6), and CT III DFS by Eq. (7). The additional five consistency tests are derived in Appendix B and are given by Eqs. (50)–(54).

The tests of the applicability of the modified DFS theory to the data of OD could fail for one or more of the following reasons: (a) because the common features of the general DFS and CBW theories are not valid for aromatic compounds, in particular that the same configurational coordinate can be assumed for the optical effect, i.e., the Stokes shift, and for the pressure effects and that the pressure acts hydrostatically in an anisotropic material; (b) because anharmonicity is only partially or inconsistently included; or (c) because of the basic differences between the general CBW theory and the unmodified DFS theory, in particular that the CBW theory includes the pressure effects on the adiabatic potentials whereas the DFS theory does not.

III. SOME GENERAL CONSIDERATIONS

In this section, we consider each of the possible reasons for the failure of the modified theory of DFS to be applicable to the OD data. We begin with (c) i.e., because of the basic differences between the general CBW theory and the unmodified DFS theory.

For the evaluation of (c), we compare a form of the CBW theory which is similar in every other aspect except for the inclusion of the pressure effects on the adiabatic potentials. In Appendix C we give the corresponding basic equations for a modified CBW theory as those given in Appendix B for the modified DFS theory. In this modified CBW theory, we assume that the adiabatic potentials are harmonic but with the harmonic frequencies pressure dependent and their ratio pressure

independent. This latter assumption means that this modified theory has the possibilities of including some of the effects of anharmonicity and the reduction of a multidimensional harmonic model to a one dimensional model. This latter point will be taken up later in this section and in Appendix D.

We find for the modified CBW theory the following equations corresponding to Eqs. (5), (6), (8), and (49):

$$a_2 + Re_2 = -(R^2 - 1)/2R\omega_0^2 , \tag{25}$$

$$a_1 + Re_1 = 0 , \tag{26}$$

$$R^2 e_1 + E_a = 0 , \tag{27}$$

and

$$\omega^2 = \omega_0^2 \left\{ 1 + \frac{2(a_1 - qR + q)}{Rq^2\omega_0^2} P + \left[\frac{2Ra_2\omega_0^2 - (R-1) - (R-1)^2}{R^2 q^2 \omega_0^4} \right] P^2 \right\}. \tag{28}$$

Equations (25)–(27) are the consistency tests for the CBW theory corresponding to CT I DFS, CT II DFS, and CT III DFS of the DFS theory which we will designate as CT I, II, and III CBW. We find, for this modified CBW theory, that the experimental data must also satisfy Eqs. (23) and (24) and, therefore, the tests of whether this modified theory is applicable to a given situation are identical to the tests of whether the modified DFS theory is applicable, i.e., tests I and II. Since the OD data fail test II, we see that the modified CBW theory is also not applicable to the OD data. Although CT I DFS and CT I CBW differ, we see that CT I CBW is not satisfied by the OD data either.
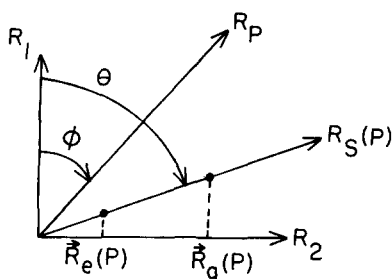
FIG. 1. Representation of the situation in which there are two local modes of importance in the description of the optical and pressure effects, where R_1 and R_2 represent the local modes, $R_s(P)$ the Stokes shift axis, and R_P the pressure effect axis.

We can conclude, therefore, that the failure of the OD data to satisfy the tests I and II is not a test of the non-inclusion of the variation of the adiabatic potentials with pressure, but is due to either reason (a) or (b) stated above and, therefore, this failure is not a test of the difference between the CBW and DFS theories. We note that if we can find a system for which tests I and II are satisfied, then we can use it to try to differentiate between the CBW and DFS theories by using the corresponding consistency tests developed for each modified theory. The corresponding five additional consistency tests for the modified CBW theory are given in Appendix C as Eqs. (69)–(73).

We now turn to the question of whether the failure of the OD data to meet the above tests could be due to the simplifying assumption common to both unmodified theories, in particular that a single configurational coordinate is general enough to deal with anisotropic materials. This assumption entails two approximations of the more general theory: first, that the directions in the full configurational space corresponding to the hydrostatic pressure effects and to the optical effects are the same and, second, that the external hydrostatic pressure acts internally in a hydrostatic manner for an anisotropic material, i.e., that the change in the site symmetry does not affect the spectrum significantly.

In order to test whether the use of a single configurational coordinate is the cause for the failure of the OD data to satisfy either modified theory, we will consider a two dimensional configurational coordinate model in which each coordinate is a local mode. We note that in some cases these local modes could be normal crystal modes. For convenience, we will assume that both the Stokes shift axis $R_s(P)$, the axis parallel to the direction along which the Stokes shift take place, and the hydrostatic pressure axis R_P, the axis parallel to the direction along which shifts due to the effects of the pressure take place, are axes contained in this two dimensional subspace. If this last condition is not fulfilled, then the argument given in Appendix D is easily generalized to a multidimensional subspace which contains these axes. Using Fig. 1, in which R_1 and R_2 are the two local modes and $R_e(P)$ and $R_g(P)$ are the positions of the minima of the excited and ground state adiabatic potential surfaces, respectively, when the hydrostatic

pressure is P, we can see that we can define the direction of $R_s(P)$, to within a sign, as the line joining $R_e(P)$ and $R_g(P)$. We then define θ as the angle between $R_s(P)$ and the R_1 axis. In addition, we can define two axes R_{eP} and R_{gP}, the hydrostatic pressure axes for the excited and ground states, respectively, to within a sign, as follows: R_{eP} is parallel to $dR_e(P)/dP$ and R_{gP} is parallel to $dR_g(P)/dP$. If R_{eP} is parallel to R_{gP}, then we can define R_P as this common axis. In addition, we define ϕ as the angle between R_P and the R_1 axis. We note that if the ratio of the coupling constants for the modes R_1 and R_2 depends on the pressure, then ϕ is pressure dependent. In both the DFS and CBW theories, the assumption is made that the coupling constants, and hence ϕ, are independent of the pressure. We note, also, that in the most general situation θ is pressure dependent.

Now the question that must be answered is whether the two dimensional harmonic model can be reduced to a one dimensional harmonic model with pressure dependent frequencies. In Appendix D we show that, in fact, this can be done. Therefore, the failure of the OD data to meet tests I and II cannot be due to the use of a single configurational coordinate, since the above result does not depend on the frequency values for the R_1 and R_2 directions being the same for each electronic state and since no significant splitting is reported due to changes in site symmetry. On the other hand, if there is a significant splitting due to changes in site symmetry, then an extension of the analysis similar to that given by Berry and Williams[18] for Jahn–Teller systems must be made.

Therefore, we are left with the reason that the OD data have failed to satisfy the above tests is that the anharmonicity is either not included or is only partially included or is inconsistently included within the framework of these modified theories, or some combination of these. If the anharmonicity were consistently and completely included in the theory, then the corresponding tests and consistency relations should fit all data, assuming other aspects of the theory are correct. Such an analysis would include the anharmonic effects on the transition energies and the most probable configuration, as well as having pressure dependent frequencies.

IV. CONCLUSION

In this work we have considered the applicability of the modified DFS theory to the data of OD. For comparison we have introduced into consideration a theory which includes the effects of pressure in the manner set forth in the theory developed by CBW, but which is modified in the same manner that the DFS theory was modified. We have concluded that the failure of the modified DFS theory is due to the limitations of the modification, in particular that the anharmonicity is not sufficiently included in this modification, since the OD data do not satisfy the applicability tests of either modified theory and since a multidimensional harmonic pressure theory can be reduced to a single dimensional theory modified to include pressure dependent force constants.

We have developed, in addition to the modified CBW theory, a pair of tests that allows us to determine if either modified theory is general enough to be applicable to a given set of data and sets of consistency tests, which, in principle, could differentiate between these theories.

The results to which these modified theories should be applicable are results for materials which behave harmonically to a good approximation, but for which the coupling to more than one mode is important. On the other hand, if only one harmonic mode is important, then ω^2 should be independent of the pressure and therefore the results given in Eqs. (11)-(16) are applicable.

In Appendix D, we have carried out the reduction from a two to a one mode configurational coordinate model, from which we can couple the pressure variation of the ω^2's for the excited and ground state of the single mode to the values of the constant ω^2's for the two modes.

We conclude, therefore, that although the modified theories are not applicable to the OD data, there could be materials and ranges of the pressure to which they are applicable. Were such data available, we should be able to differentiate between the theories of CBW and DFS using the relationships between the experimental results developed here. However, the more likely differentiation between these theories will be made based on versions which fully include anharmonicity.

ACKNOWLEDGMENTS

APPENDIX A: NOTATION

The adiabatic potential for the ground state at zero pressure is

$$V_g = \tfrac{1}{2}\omega^2 Q^2 \tag{29}$$

and for the excited state is

$$V_e = E_0 + \tfrac{1}{2}\omega'^2 (Q - q)^2 . \tag{30}$$

R and N are defined as

$$R = (\omega'/\omega)^2 \tag{31}$$

and

$$N = (8kT \ln 2)^{1/2} .$$

$\mathscr{E}_a$ and $\delta\mathscr{E}_a$ are the optical absorption energy peak position and its shift, respectively, and $\mathscr{E}_e$ and $\delta\mathscr{E}_e$ are the optical emission energy peak position and its shift, respectively. We assume that the experimental data for $\delta\mathscr{E}_a$ and $\delta\mathscr{E}_e$ can be fitted to

$$\delta\mathscr{E}_a = a_1 P + a_2 P^2 \tag{32}$$

and

$$\delta\mathscr{E}_e = e_1 P + e_2 P^2 , \tag{33}$$

respectively. ϵ_a and $\delta\epsilon_a^2$ are the optical absorption peak half-width and the shift in its square and ϵ_e and $\delta\epsilon_e^2$ are the optical emission peak half-width and the shift in its square, respectively. We assume that the experimental data for $\delta\epsilon_a^2$ and $\delta\epsilon_e^2$ can be fitted to

$$\frac{\delta\epsilon_a^2}{N^2} = 2E_a P + D_a P^2 \tag{34}$$

and

$$\frac{\delta\epsilon_e^2}{N^2} = 2E_e P + D_e P^2 , \tag{35}$$

respectively. The assumption made by ODD[3] is that

$$\omega^2 = \omega_0^2 (1 + b_1 P + b_2 P^2) , \tag{36}$$

and that R is independent of the pressure.

APPENDIX B: DERIVATION OF THE CONSISTENCY TESTS FOR THE MODIFIED DRICKAMER, FRANK, AND SLICHTER THEORY

Both T and OD have given the basic theoretical form for $\delta\mathscr{E}_a$, $\delta\mathscr{E}_e$, $\delta\epsilon_a^2$, and $\delta\epsilon_e^2$. They are

$$\delta\mathscr{E}_a = RqP + \frac{(R-1)}{2\omega^2} P^2 + \frac{Rq^2}{2} (\omega^2 - \omega_0^2) , \tag{37}$$

$$\delta\mathscr{E}_e = \frac{qP}{R} + \frac{(R-1)}{2R^2\omega^2} P^2 - \frac{q^2}{2} (\omega^2 - \omega_0^2) , \tag{38}$$

$$\frac{\delta\epsilon_a^2}{N^2} = R^2 q^2 (\omega^2 - \omega_0^2) + 2R(R-1) qP + \frac{(R-1)^2 P^2}{\omega^2} , \tag{39}$$

and

$$\frac{\delta\epsilon_e^2}{N^2} = \frac{1}{R^3}\left[R^2 q^2 (\omega^2 - \omega_0^2) + 2R(R-1) qP + \frac{(R-1)^2 P^2}{\omega^2} \right] . \tag{40}$$

In Eqs. (39) and (40), $\delta\epsilon_a^2$ and $\delta\epsilon_e^2$ are found from $\delta\epsilon_a$ and $\delta\epsilon_e$, respectively, by using the following relationship:

$$\delta\epsilon^2 = \epsilon^2 - (\epsilon^0)^2 = (\delta\epsilon)^2 + 2\epsilon^0 \delta\epsilon ,$$

where ϵ^0 is the half-width at atmospheric pressure.

It is immediately obvious from Eqs. (39) and (40) that

$$R^3 = \frac{\delta\epsilon_a^2 / N^2}{\delta\epsilon_e^2 / N^2} . \tag{41}$$

Using Eqs. (32), (33), (37), and (38), we find after simplification that

$$R^2 q^2 \omega^4 + [2(Rq - a_1) RP - 2a_2 RP^2 - R^2 q^2 \omega_0^2] \omega^2 + (R-1) RP^2$$
$$= 0 \tag{42}$$

and

$$R^2 q^2 \omega^4 + [2(Re_1 - q)RP + 2e_2 R^2 P^2 - R^2 q^2 \omega_0^2] \omega^2 - (R-1)P^2$$
$$= 0 . \tag{43}$$

Since these are independent processes for the same material parameters, we would expect that there is a unique ω^2 for the material which must be a solution of both Eqs. (42) and (43). Therefore, if we solve Eqs. (42) and (43) for ω^2 and expand the square root in a power series in P keeping terms up to second order in P, and note that the solutions having a negative sign in front of

the square root go to zero when P goes to zero and that the other solutions go to ω_0^2, then we can reject the negative signed solutions and set the positive signed solutions equal to one another. This gives

$$\omega^2 = \omega_0^2 \left[1 + \frac{2(a_1 - Rq)P}{Rq^2\omega_0^2} + \left(\frac{2a_2\omega_0^2 - R + 1}{Rq^2\omega_0^4} \right)P^2 \right]$$

$$= \omega_0^2 \left[1 + \frac{2(q - Re_1)P}{Rq^2\omega_0^2} - \left(\frac{2e_2\omega_0^2 R^2 - R + 1}{R^2 q^2 \omega_0^4} \right)P^2 \right].$$
(44)

Since this equality must be true for all P, we find that

$$a_2 + Re_2 = (R^2 - 1)/2R\omega_0^2 \tag{45}$$

and

$$a_1 + Re_1 = (R + 1)q . \tag{46}$$

These last two equations are the consistency tests I DFS and II DFS given in the text. We can continue this type of analysis using Eqs. (34), (35), (39), and (40); we then find the following strings of equalities:

$$(a_1 - Rq)R = (q - Re_1)R = E_a - R(R-1)q = R^3 E_e - R(R-1)q \tag{47}$$

and

$$2Ra_2\omega_0^2 - R(R-1) = -2R^2\omega_0^2 e_2 + (R-1)$$
$$= D_a\omega_0^2 - (R-1)^2 = R^3 D_e\omega_0^2 - (R-1)^2 . \tag{48}$$

The theoretical unknowns in these equations are R, q, and ω_0^2. By elimination of these quantities, we find the following additional consistency tests (CT):

CT III DFS:

$$R^2 e_1 + E_a = R^2 q ; \tag{49}$$

CT IV DFS:

$$(E_a E_e)^{1/3}(E_a^{1/3} + E_e^{1/3}) = a_1 - e_1 ; \tag{50}$$

CT V DFS:

$$D_a E_e = D_e E_a ; \tag{51}$$

CT VI DFS:

$$(D_a D_e)^{1/3}(D_a^{1/3} + D_e^{1/3}) = 2(a_2 - e_2) ; \tag{52}$$

CT VII DFS:

$$\frac{R(R-1)}{D_a + 2Re_2} > 0 ; \tag{53}$$

and CT VIII DFS:

$$\frac{R^2 - 1}{a_2 + Re_2} > 0 . \tag{54}$$

We also find by using Eqs. (37)–(40) that

$$q^2 \omega_0^2 (R+1) = \frac{4(\delta\mathcal{E}_a - \delta\mathcal{E}_e)}{\frac{\delta\epsilon_a^2}{\epsilon_a^2(0)} + \frac{\delta\epsilon_e^2}{\epsilon_e^2(0)}} . \tag{55}$$

APPENDIX C: DERIVATION OF CONSISTENCY TESTS FOR THE MODIFIED CURIE, BERRY, AND WILLIAMS THEORY

Using the harmonic approximation in the CBW theory, we can find that

$$\delta\mathcal{E}_a = \tfrac{1}{2} Rq^2(\omega^2 - \omega_0^2) + q(R-1)P$$
$$+ \frac{1}{2R\omega^2}[(R-1)^2 - (R-1)]P^2 , \tag{56}$$

$$\delta\mathcal{E}_e = -\tfrac{1}{2} q^2(\omega^2 - \omega_0^2) - \frac{q(R-1)P}{R}$$
$$- \frac{1}{2R\omega^2}[R(R-1) + (R-1)^2]P^2 , \tag{57}$$

$$\frac{\delta\epsilon_a^2}{N^2} = R^2 q^2(\omega^2 - \omega_0^2) + 2qR(R-1)P + \frac{(R-1)^2 P^2}{\omega^2} , \tag{58}$$

and

$$\frac{\delta\epsilon_e^2}{N^2} = \frac{1}{R^3}\left[R^2 q^2(\omega^2 - \omega_0^2) + 2qR(R-1)P + \frac{(R-1)^2 P^2}{\omega^2} \right] . \tag{59}$$

We again see immediately that Eqs. (58) and (59) imply that

$$R^3 = \frac{\delta\epsilon_a^2/N^2}{\delta\epsilon_e^2/N^2} . \tag{60}$$

Using Eqs. (32), (33), (56), and (57), we find after simplification that

$$R^2 q^2 \omega^4 + [2Rq(R-1)P - 2Ra_1 P - 2Ra_2 P^2 - R^2 q^2 \omega_0^2]$$
$$\times \omega^2 + [(R-1)^2 - (R-1)]P^2 = 0 \tag{61}$$

and

$$R^2 q^2 \omega^4 + [2Rq(R-1)P + 2R^2 e_1 P + 2R^2 e_2 P^2 - R^2 q^2 \omega_0^2]$$
$$\times \omega^2 + [(R-1)^2 - R(R-1)]P^2 = 0 . \tag{62}$$

Here again, we find the properties of the solutions to Eqs. (61) and (62) for ω^2 are the same as stated for the solutions of Eqs. (42) and (43). We therefore reject the negative signed solutions and set the positive signed solutions equal to one another. This gives

$$\omega^2 = \omega_0^2 \left\{ 1 + \frac{2[a_1 - q(R-1)]}{Rq^2\omega_0^2} P \right.$$
$$+ \left[\frac{2Ra_2\omega_0^2 + (R-1) - (R-1)^2}{R^2 q^2 \omega_0^4} \right] P^2 \right\}$$
$$= \omega_0^2 \left\{ 1 - \frac{2[Re_1 + q(R-1)]}{Rq^2\omega_0^2} P \right.$$
$$\left. - \left[\frac{2R^2 e_2\omega_0^2 + R(R-1) + (R-1)^2}{R^2 q^2 \omega_0^4} \right] P^2 \right\} . \tag{63}$$

From Eq. (63), we find that

$$a_2 + Re_2 = -(R^2 - 1)/2R\omega_0^2 \tag{64}$$

and

$$a_1 + Re_1 = 0 . \tag{65}$$

These last two equations are the consistency tests CT I CBW and II CBW given in the text. We can continue this type of analysis using Eqs. (34), (35), (58), and (59); we then find the following strings of equalities:

$$R[a_1 - q(R-1)] = -R[Re_1 + q(R-1)] = E_a - qR(R-1)$$

$$= R^3 E_e - qR(R-1) \tag{66}$$

and

$$2Ra_2\omega_0^2 + (R-1) - (R-1)^2 = 2R^2 e_2\omega_0^2 - R(R-1) - (R-1)^2$$

$$= D_a\omega_0^2 - (R-1)^2$$

$$= R^3 D_e\omega_0^2 - (R-1)^2 . \tag{67}$$

The theoretical unknowns in these equations are again R, q, and ω_0^2. By eliminating these quantities, we find the following additional consistency tests (CT):

CT III CBW:

$$R^2 e_1 + E_a = 0 ; \tag{68}$$

CT IV CBW:

$$(E_a E_e)^{1/3}(E_a^{1/3} + E_e^{1/3}) = a_1 - e_1 ; \tag{69}$$

CT V CBW:

$$D_a E_e = D_e E_a ; \tag{70}$$

CT VI CBW:

$$(D_a D_e)^{1/3}(D_a^{1/3} + D_e^{1/3}) = 2(a_2 - e_2) ; \tag{71}$$

CT VII CBW:

$$\frac{R(R-1)}{D_a + 2R^2 e_2} < 0 ; \tag{72}$$

and CT VIII CBW:

$$\frac{R^2 - 1}{a_2 + Re_2} < 0 . \tag{73}$$

We also find by using Eqs. (56) through (59) to eliminate P that

$$q^2\omega_0^2(R+1) = \frac{4(\delta\mathcal{E}_a - \delta\mathcal{E}_e)}{\frac{\delta\epsilon_a^2}{\epsilon_a^2(0)} + \frac{\delta\epsilon_e^2}{\epsilon_e^2(0)}} . \tag{74}$$

APPENDIX D: REDUCTION FROM THE TWO-DIMENSIONAL TO ONE-DIMENSIONAL MODEL

The description of the two-dimensional model is given by the following equations for the adiabatic potentials and the pressure dependence of the components of the vector joining the minima of these adiabatic potential surfaces:

$$V_g = \tfrac{1}{2}\omega_1^2 Q_1^2 + \tfrac{1}{2}\omega_2^2 Q_2^2 , \tag{75}$$

$$V_e = \tfrac{1}{2}\omega_1'^2(Q_1 - q_1)^2 + \tfrac{1}{2}\omega_2'^2(Q_2 - q_2)^2 + E_0 , \tag{76}$$

and

$$q_i(P) = q_i(0) + P\left(\frac{1}{\omega_i^2} - \frac{1}{\omega_i'^2}\right) , \quad i = 1, 2 . \tag{77}$$

The description of the one-dimensional model is given by the corresponding equations as follows:

$$V_g = \tfrac{1}{2}\omega^2(P) Q^2 , \tag{78}$$

$$V_e = \tfrac{1}{2}\omega'^2(P)(Q - q)^2 + E_0 , \tag{79}$$

and

$$q(P) = q(0) + P\left[\frac{1}{\omega^2(P)} - \frac{1}{\omega'^2(P)}\right] . \tag{80}$$

We find that in making the transformation from the two dimensional to the one dimensional model that the frequencies, in general, must be pressure dependent in the one dimensional model. However, in the present situation, this is not a limitation, since we are considering the modified one-dimensional harmonic pressure theories of CBW and DFS.

To find the corresponding one-dimensional description of the two-dimensional description, we must find a transformation from Eqs. (75)–(77) to Eqs. (78)–(80). We note that it is straightforward to find a transformation from Eqs. (75) and (76) to Eqs. (78) and (79); however, in the case of the pressure theory, we have the additional condition of satisfying Eq. (80). We see that this equation can always be satisfied if the transformation includes a pressure dependent scale for the one-dimensional configurational coordinate.

The form of the transformation is therefore chosen to be

$$(Q_1, Q_2) = Q(y_1(P), y_2(P)) , \tag{81}$$

and

$$[q_1(P), q_2(P)] = q(P)[y_1(P), y_2(P)] , \tag{82}$$

where

$$y_i(P) = y_i + \lambda_i P + \Lambda_i P^2 , \quad i = 1, 2 . \tag{83}$$

Since these are normal coordinates, then

$$q^2(P) = \frac{q_1^2(P) + q_2^2(P)}{y_1^2(P) + y_2^2(P)} , \tag{84}$$

$$V_e = \tfrac{1}{2}\omega'^2(P)[Q - q(P)]^2 + E_0 , \tag{85}$$

and

$$V_g = \tfrac{1}{2}\omega^2(P) Q^2 , \tag{86}$$

where

$$\omega'^2(P) = y_1^2(P) \omega_1'^2 + y_2^2(P) \omega_2'^2 \tag{87}$$

and

$$\omega^2(P) = y_1^2(P) \omega_1^2 + y_2^2(P)\omega_2^2 . \tag{88}$$

The pressure dependence of $q(P)$ has the form

$$q(P) = q + P\left[\frac{1}{\omega^2(P)} - \frac{1}{\omega'^2(P)}\right] , \tag{89}$$

where $q = q(0)$ and where the q_i's pressure dependence is given by Eq. (77).

By choosing this form of the transformation, we have correctly transformed from Eqs. (75) and (76) to Eqs. (78) and (79), independent of the choice for y_i, λ_i, and Λ_i, $i = 1, 2$. We now have to determine these six unknowns and have only three equations that must be satisfied by them. These three equations are given by the conditions that the first three coefficients in the power series expansion in P of the left-hand side of the following equation must be zero:

$$q^2(P) - \left\{q + P\left[\frac{1}{\omega^2(P)} - \frac{1}{\omega'^2(P)}\right]\right\}^2 = 0 , \tag{90}$$

where $q^2(P)$ is given by Eq. (84). Therefore, we can add three arbitrary conditions on the y's, λ's, and Λ's

in order to uniquely determine them. We will consider two cases. Case I will be the case where R is independent of P, and case II will be the case where Q is parallel to the line joining the minima of the adiabatic potential surfaces for all values of P.

For case I, we make R independent of the pressure by choosing

$$y_1(P) = y_1(1 + \lambda P + \Lambda P^2) \qquad (91)$$

and

$$y_2(P) = y_2(1 + \lambda P + \Lambda P^2) . \qquad (92)$$

We find that (y_1, y_2) must be a unit vector and that

$$\lambda = \frac{q_1}{q^2}\left(\frac{1}{\omega_1^2} - \frac{1}{\omega_1'^2}\right) + \frac{q_2}{q^2}\left(\frac{1}{\omega_2^2} - \frac{1}{\omega_2'^2}\right) - \frac{1}{q}\left(\frac{1}{\omega^2} - \frac{1}{\omega'^2}\right) , \qquad (93)$$

and

$$\Lambda = \frac{-\lambda^2}{2} + \frac{1}{2q^2}\left(\frac{1}{\omega_1^2} - \frac{1}{\omega_1'^2}\right)^2 + \frac{1}{2q^2}\left(\frac{1}{\omega_2^2} - \frac{1}{\omega_2'^2}\right)^2$$

$$- \frac{1}{2q^2}\left(\frac{1}{\omega^2} - \frac{1}{\omega'^2}\right)^2 + \frac{2y_1^2\lambda}{q}\left[\frac{(\omega_1^2 - \omega^2)}{\omega^4} - \frac{(\omega_1'^2 - \omega'^2)}{\omega'^4}\right]$$

$$+ \frac{2y_2^2\lambda}{q}\left[\frac{(\omega_2^2 - \omega^2)}{\omega^4} - \frac{(\omega_2'^2 - \omega'^2)}{\omega'^4}\right] , \qquad (94)$$

where $\omega^2 = \omega^2(0)$ and $\omega'^2 = \omega'^2(0)$. In this case R is given by

$$R = \left[\frac{\omega'(P)}{\omega(P)}\right]^2 = \frac{y_1^2\,\omega_1'^2 + y_2^2\,\omega_2'^2}{y_1^2\,\omega_1^2 + y_2^2\,\omega_2^2} . \qquad (95)$$

We can choose any direction in the two dimensional space for the Q direction; however, in the zero pressure theory the most obvious direction is the direction parallel to the line joining the minima of the adiabatic potential surfaces for zero pressure, from which we have

$$y_1 = \frac{q_1}{q} \quad\text{and}\quad y_2 = \frac{q_2}{q} .$$

For case II, this case is described by the following equations:

$$y_1(P)\,q(P) = q_1(P) \qquad (96)$$

and

$$y_2(P)\,q(P) = q_2(P) . \qquad (97)$$

We note that if Eqs. (96) and (97) are satisfied, then Eq. (80) will be satisfied. The solution of Eqs. (96) and (97) is

$$y_i = q_i / q , \qquad (98)$$

$$\lambda_i = \frac{1}{q}\left(\frac{1}{\omega_i^2} - \frac{1}{\omega_i'^2}\right) - \frac{q_i}{q^2}\left(\frac{1}{\omega^2} - \frac{1}{\omega'^2}\right) , \qquad (99)$$

$$\Lambda_i = -\left(\frac{1}{\omega^2} - \frac{1}{\omega'^2}\right)\frac{\lambda_i}{q} + \frac{2q_i}{q^3}$$

$$\times \left[\frac{q_1\lambda_1\omega_1^2 + q_2\lambda_2\omega_2^2}{\omega^4} - \frac{q_1\lambda_1\omega_1'^2 + q_2\lambda_2\omega_2'^2}{\omega'^4}\right] , \qquad (100)$$

where $i = 1, 2$,

$$\omega^2 = \omega^2(0) = (q_1^2\omega_1^2 + q_2^2\omega_2^2)/q^2 ,$$

and

$$\omega'^2 = \omega'^2(0) = (q_1^2\omega_1'^2 + q_2^2\omega_2'^2)/q^2 .$$

In this case we find that R is pressure dependent, unless either of the following conditions are met:

$$\frac{\omega_1^2}{\omega_1'^2} = \frac{\omega_2^2}{\omega_2'^2} \qquad (101)$$

or

$$q_1\left(\frac{1}{\omega_2^2} - \frac{1}{\omega_2'^2}\right) = q_2\left(\frac{1}{\omega_1^2} - \frac{1}{\omega_1'^2}\right) . \qquad (102)$$

Case I corresponds to the assumption used by ODD, i.e., that R is independent of the pressure, and this seems to be the appropriate form of the reduction to use with the DFS theory, since in the DFS theory the adiabatic potential surfaces are assumed independent of the pressure, which implies that θ is independent of the pressure which is the situation in case I. See Fig. 1 for the definition of θ. However, for the CBW theory, case II would be the appropriate choice, since the adiabatic potential surfaces are pressure dependent. Note also that in this reduction we have assumed that the set of normal modes is independent of the pressure, which is not always the case.

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