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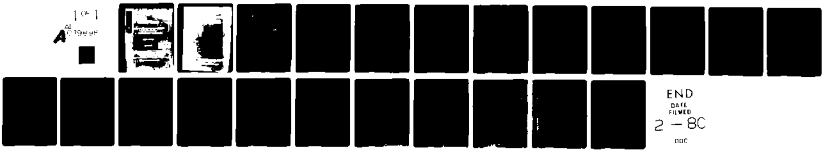

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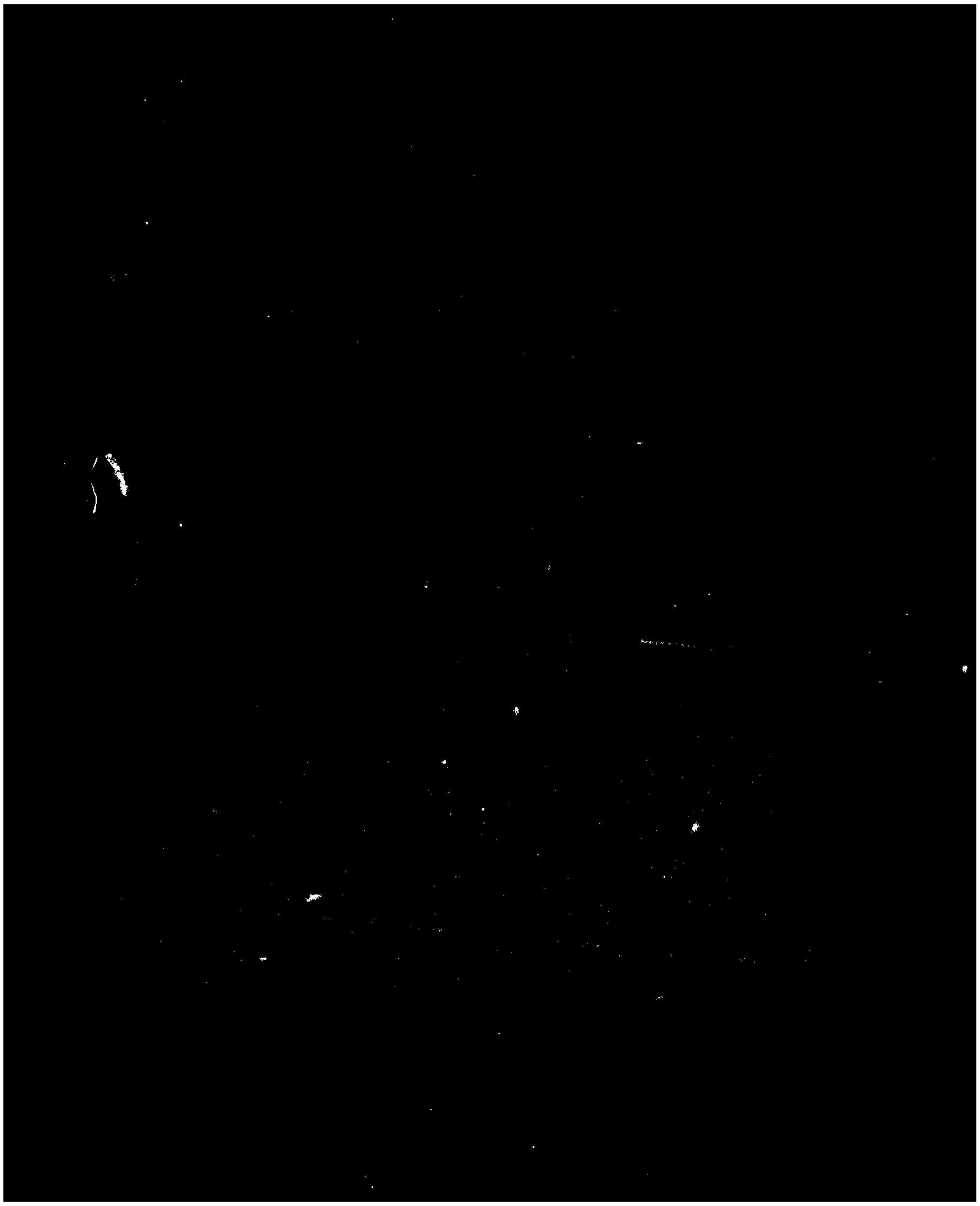

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The effects of high pressure on electronic spectra are treated on the basis of a Morse potential by a method analogous to that used in deriving the well-known Drickamer model. Expressions are presented for evaluating configuration-coordinate parameters for spectroscopic data.

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I. INTRODUCTION

A previous paper[1,1a] examined the harmonic-oscillator model of Drickamer et al[2,3] for the effects of high pressure on molecular, electronic spectra. The parameterization of the model by Okamoto et al[4] was reformulated to conform with the conclusions of Lin[5] and tested on the data of Okamoto and Drickamer.[6] Although the reformulation improved the agreement, the results were not entirely satisfying. As one of the possible causes for discrepancies, I suggested anharmonicity. For the next level of sophistication in this direction, the incorporation of the Morse potential suggests itself.

The present paper derives expressions analogous to those of Reference 1, based upon the Morse potential rather than the harmonic oscillator. Since Lin[5] has shown that his quantum-mechanical treatment leads to the Drickamer equations when the same assumptions are made, we shall follow Drickamer's simpler and more transparent approach here. Part II summarizes the approach and introduces the basic equations that will be required. The expressions for peak height are derived in Part III, and those for bandwidth in Part IV. Part V casts the expressions in a compact form suitable for experimental testing, and Part VI makes concluding remarks. The Appendix lists several expansions in Maclaurin series that are used in the text.

II. GENERAL CONSIDERATIONS

We assume that pressure couples to a Morse potential along a single configuration coordinate, viz., volume. The potential functions of the ground and excited electronic states are then given, respectively, by

$$V = D(1 - e^{-\beta Q})^2 + cpQ \qquad (2.1)$$

and

$$V^* = D^*(1 - e^{-\beta^*(Q-q)})^2 + rcpQ + E_0, \qquad (2.2)$$

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[1] Tompkins, R.C., J. Chem. Phys. 69, 579 (1978).

[1a] Tompkins, R.C., Effects of High Pressure on Molecular Electronic Spectra: A Comparison of Models, BRL R No. 2014, (1977).(A045414)

[2] Drickamer, H.G., Frank, C.W., and Slichter, C.P., Proc. Nat. Acad. Sci. (USA) 69, 933 (1972).

[3] Drickamer, H.G., and Frank, C.W., "Electronic Transitions and the High Pressure Chemistry and Physics of Solids, "London: Chapman and Hall (1943).

[4] Okamoto, B.Y., Drotning, W.E., and Drickamer, H.G., Proc. Nat. Acad. Sci. (USA) 71, 2671 (1973).

[5] Lin, S.H. J. Chem. Phys, 59, 4458 (1973)

[6] Okamoto, B.Y., and Drickamer, H.G., J. Chem. Phys. 61, 2870 (1974).

where D, β, D*, β*, c are constants, p is pressure, Q is the configuration coordinate, r is the ratio of the coupling constant in the excited state to that in the ground state, and E_o and q are the energy and coordinate separations, respectively, between the potential minima. Note that when the Morse function is reduced to the harmonic function, we obtain ω^2 of References 1-6 as $2\beta^2D$.

We shall obtain an expression for the optical absorption energy by projecting the minimum of eq. (2.1) upon eq. (2.2) in accordance with the Franck-Condon principle, and _mutatis mutandis_ for emission. We shall obtain the bandwidths by projecting the terminal points of oscillation of the lowest vibrational level.

Differentiation of eqs. (2.1) and (2.2) yields

$$\partial V/\partial Q = 2\beta D e^{-\beta Q}(1 - e^{-\beta Q}) + cp \tag{2.3}$$

and

$$\partial V^*/\partial Q = 2R\rho\beta D\gamma e^{-\rho\beta Q}(1 - \gamma e^{-\rho\beta Q}) + rcp, \tag{2.4}$$

where $R = D^*/D$, $\rho = \beta^*/\beta$, and $\gamma = e^{\rho\beta q}$. Setting these expressions equal to zero and solving as quadratic equations in the exponentials, we obtain

$$e^{-\beta Q_m} = \tfrac{1}{2}(1 + \sqrt{1+2cp/\beta D}\,) \tag{2.5}$$

and

$$e^{-\rho\beta Q^*_m} = (1 + \sqrt{1+2rcp/R\rho\beta D})/2\gamma. \tag{2.6}$$

Hence

$$Q_m = [\log 2 - \log(1 + \sqrt{1+2cp/\beta D})]/\beta \tag{2.7}$$

and

$$Q^*_m = q + [\log 2 - \log(1 + \sqrt{1+2rcp/R\rho\beta D})]/\rho\beta. \tag{2.8}$$

The potential minima are then

$$V_m = \tfrac{1}{2}D(1 - \sqrt{1+2cp/\beta D}) + \frac{1 + 2[\log 2 - \log(1 + \sqrt{1+2cp/\beta D})]}{2\beta}cp \tag{2.9}$$

and

$$V^*_m = \tfrac{1}{2}RD(1 - \sqrt{1+2rcp/R\rho\beta D}) + crqp + E_o \\ + \frac{1 + 2[\log 2 - \log(1 + \overline{2rcp/R\quad D)}]}{2\rho\beta}\,rcp. \tag{2.10}$$

It will be convenient to obtain at this point certain other quantities that will be required in the sequel. Differentiation of eqs. (2.9) and (2.10) with respect to pressure yields

$$V'_m(p) = 2\beta DQ'_m e^{-\beta Q_m}(1 - e^{-\beta Q_m}) + c(Q'_m p + Q_m) \tag{2.11}$$

and

$$V^{*\prime}_m(p) = 2R\rho\beta D\gamma Q^{*\prime}_m e^{-\rho\beta Q^*_m}(1 - \gamma e^{-\rho\beta Q^*_m}) + rc(Q^{*\prime}_m p + Q^*_m). \tag{2.12}$$

Evaluating eqs. (2.7) - (2.12) at p=0, we obtain

$$Q_m(0) = 0, \tag{2.13}$$

$$V_m(0) = 0, \tag{2.14}$$

$$V'_m(0) = 0, \tag{2.15}$$

$$Q^*_m(0) = q, \tag{2.16}$$

$$V^*_m(0) = E_o, \tag{2.17}$$

and

$$V^{*\prime}_m(0) = rcq. \tag{2.18}$$

(We shall not require $Q'_m(0)$ or $Q^{*\prime}_m(0)$.)

III. PEAK HEIGHT

A. Absorption.

We project the potential minimum of the ground state upon the potential function of the excited state by substituting eq. (2.7) into eq. (2.2):

$$V^*(Q_m) = RD[1 - 2\gamma(1 + \sqrt{1+2cp/\beta D})^{\rho}/2^{\rho} + \gamma^2(1 + \sqrt{1+2cp/\beta D})^{2\rho}/2^{2\rho}] \tag{3.1}$$

$$+ rc[\log 2 - \log(1 + \sqrt{1+2cp/\beta D})]p/\beta + E_o.$$

Subtraction of eq. (2.9) yields the optical absorption energy, It will be convenient to obtain at this point certain other quantities that will be required in the sequel. Differentiation of eqs. (2.9) and (2.10) with respect to pressure yields

$$V'_m(p) = 2\beta D Q'_m e^{-\beta Q_m}(1 - e^{-\beta Q_m}) + c(Q'_m p + Q_m) \tag{2.11}$$

and

$$V^{*\prime}_m(p) = 2R\rho\beta D\gamma Q^{*\prime}_m e^{-\rho\beta Q^*_m}(1 - \gamma e^{-\rho\beta Q^*_m}) + rc(Q^{*\prime}_m p + Q^*_m). \tag{2.12}$$

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$$+ rc[\log 2 - \log(1 + \sqrt{1+2cp/\beta D})]p/\beta + E_o. \tag{3.1}$$

Subtraction of eq. (2.9) yields the optical absorption energy,

$$\mathcal{E}_a = V^*(Q_m) - V_m$$

$$= RD\gamma 2^{-\rho}(1 + \sqrt{1+2cp/\beta D})^{\rho}[2^{-\rho}\gamma(1 + \sqrt{1+2cp/\beta D})^{\rho} - 2] + K \tag{3.2}$$

$$+\tfrac{1}{2}D\sqrt{1+2cp/\beta D} - cp/2\beta + (cp/\beta)(1-r)[\log(1 + \sqrt{1+2cp/\beta D}) - \log 2],$$

where $K = E_o + D(R - \tfrac{1}{2})$, which is independent of pressure.

The experiments of Okamoto and Drickamer[6,7] have provided convincing evidence that $\mathcal{E}_a$ is a quadratic function of p. Therefore, we shall expand eq. (3.2) in a Maclaurin series to second order in p, using eqs. (A.1), (A.2), and (A.3). After subtracting the energy at zero pressure, we obtain the pressure shift of the absorption peak,

$$\delta\mathcal{E}_a = \frac{R\rho\gamma(\gamma - 1)}{\beta}cp + \frac{R\rho\gamma[\rho(2\gamma - 1) - 3(\gamma - 2)] + (1 - 2r)}{4\beta^2 D}c^2p^2. \tag{3.3}$$

B. Emission.

We project the potential *minimum* of the excited state upon the potential function of the ground state by substituting eq. (2.8) into eq. (2.1):

$$V(Q_m^*) = D[1 - 2\left(\frac{1 + \sqrt{1+2rcp/R\rho\beta D}}{2\gamma}\right)^{1/\rho} + \left(\frac{1 + \sqrt{1+2rcp/R\rho\beta D}}{2\gamma}\right)^{2/\rho}] \tag{3.4}$$

$$+ cpq + (cp/\rho\beta)[\log 2 - \log(1 + \sqrt{1+2rcp/R\rho\beta D})] .$$

Subtraction from eq. (2.10) yields the optical emission energy,

$$\mathcal{E}_e = D\gamma^{-1/\rho}\left(\frac{1 + \sqrt{1+2rcp/R\rho\beta D}}{2}\right)^{1/\rho}[2 - \left(\frac{1 + \sqrt{1+2rcp/R\rho\beta D}}{2\gamma}\right)^{1/\rho}]$$

$$- \tfrac{1}{2}RD\sqrt{1+2rcp/R\rho\beta D} + rcp/2\beta D + (r - 1)cqp \tag{3.5}$$

$$+ (cp/\rho\beta)(r - 1)[\log 2 - \log(1 + \sqrt{1+2rcp/R\rho\beta D})] + K',$$

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[7] Okamoto, B.Y., and Drickamer, H.G., J. Chem. Phys., 61, 2870 (1974).

where $K' = E_o + (R/2 - 1)D$, which is independent of pressure. Again we expand in Maclaurin series to second order in p, using eqs. (A.4), (A.5), and (A.6), and subtract the energy at zero pressure. The pressure shift of the emission peak is then,

$$\delta\mathcal{E}_e = \frac{r\gamma^{-1/\rho}(1 - \gamma^{-1/\rho}) + (r - 1)\, R\rho^2\beta q}{R\rho^2\beta}cp$$

$$+ \frac{r\,\gamma^{-1/\rho}\{r[(1 - 2\gamma^{-1/\rho} - 3\rho(1 - \gamma^{-1/\rho})] + R(2-r)\}}{4R^2\rho^2\beta^2 D}c^2p^2 \,. \tag{3.6}$$

IV. BANDWIDTH

A. Absorption.

Let us represent the terminal points of oscillation in the lowest vibrational state of the electronic ground state by Q_+ and Q_- (collectively, $Q_\pm$). Then the bandwidth is given by the energy difference between their projections upon the potential function of the excited state:

$$E^*_+ - E^*_- = RD[\,(1-\gamma\phi^\rho_+)^2 - (1-\gamma\phi^\rho_-)^2] + rc(Q_+-Q_-)p, \tag{4.1}$$

where

$$\phi_\pm = e^{-\beta Q_\pm} \,. \tag{4.2}$$

It will be convenient to rearrange eq. (4.1) in the form

$$E^*_+-E^*_- = RD\gamma[\gamma(\phi^{2\rho}_+-\phi^{2\rho}_-) - 2(\phi^\rho_+ - \phi^\rho_-)] + rc(Q_+-Q_-)p. \tag{4.3}$$

Following the experimental evidence of References 6 and 7 that the bandwidth is a linear function of pressure, let us expand the bandwidth in a Maxlaurin series to first order in p:

$$E^*_+-E^*_- = (E^*_+-E^*_-)_0 + (E^*_+-E^*_-)'_0 p, \tag{4.4}$$

where a zero subscript denotes evaluation at p=0, and a prime denotes a derivative with respect to p. Differentiation of eq. (4.3) yields

$$(E_+^* - E_-^*)' = 2RD\rho\gamma[\gamma(\phi_+^{2\rho-1}\phi_+' - \phi_-^{2\rho-1}\phi_-') - (\phi_+^{\rho-1}\phi_+' - \phi_-^{\rho-1}\phi_-')]$$

$$+ rc(Q_+ - Q_-) + rc(Q_+' - Q_-')p. \tag{4.5}$$

The energy at the terminal points of oscillation can be expressed by

$$D(1 - \phi_\pm)^2 + cQ_\pm p = V_m + kT/2, \tag{4.6}$$

where k is the Boltzmann constant and T is temperature. Although this transcendental equation cannot be solved analytically for $Q_\pm$, we can evaluate it at p=0 with the aid of eq. (2.14). Defining $\alpha = \sqrt{kT/2D}$, we have

$$1 - \phi_\pm(0) = \pm\alpha \tag{4.7}$$

or

$$\phi_\pm(0) = 1 \mp \alpha \tag{4.8}$$

and

$$Q_\pm(0) = -\log(1 \mp \alpha)/\beta\ . \tag{4.9}$$

The signs have been chosen such that $Q_+(0) > 0$ and $Q_-(0) < 0$.

The implicit differentiation of eqs. (4.2) and (4.6) with respect to p yields

$$\phi_\pm' = -\beta Q_\pm' e^{-\beta Q_\pm} \tag{4.10}$$

and

$$-2D\phi_\pm'(1 - \phi_\pm) + cQ_\pm' p + cQ_\pm = V_m'\ . \tag{4.11}$$

Recalling eq. (2.15), we obtain

$$\phi_\pm'(0) = \pm \frac{c \log(1 \mp \alpha)}{2\alpha\beta D} \tag{4.12}$$

and

$$Q_\pm'(0) = -\frac{\phi_\pm'(0)}{\beta\phi_\pm(0)}\ . \tag{4.13}$$

Evaluation of eq. (4.3) and (4.5) at p=0 introduces complicated functions of α. Since the energy at the potential minimum is certainly much less than the dissociation energy, D, $\alpha \ll 1$. Therefore, we can simplify by means of Maclaurin series in α (eqs. (A.7), (A.8), and (A.9)), retaining only the first nonvanishing power of α. Thus, we obtain

$$(E_+^* - E_-^*)_0 = 4RD\alpha\gamma\rho(1 - \gamma) \; . \tag{4.14}$$

and

$$(E_+^* - E_-^*)_0' = (Rc\alpha\gamma\rho/\beta)[2\rho - 3 - \gamma(4\rho - 3)] + 2rc\alpha/\beta. \tag{4.15}$$

Substituting eqs. (4.14) and (4.15) into eq. 4.4, we have

$$E_+^* - E_-^* \cong 4RD\alpha\gamma\rho(1 - \gamma) + (c\alpha/\beta)\;\{R\gamma\rho[2\rho-3 - \gamma(4\rho-3)] + 2r\}p. \tag{4.16}$$

The Gaussian half-width is obtained by multiplying by $(2 \log 2)^{\frac{1}{2}}$:

$$\varepsilon_a = 4R\gamma\rho(1-\gamma)(kTD \log 2)^{\frac{1}{2}} + [c(kT \log 2)^{\frac{1}{2}}/\beta\sqrt{D}]\;\{R\gamma\rho[2\rho-3-\gamma(4\rho-3)] + 2r\}p. \tag{4.17}$$

B. Emission.

Analogous to eq. (4.1) we have

$$E_+ - E_- = D[(1 - \phi_+^{*\,1/\rho})^2 - (1 - \phi_-^{\,1/\rho})^2] + c(Q_+^* - Q_-^*)p \; , \tag{4.18}$$

where

$$\phi_\pm^* = e^{-\rho\beta Q_\pm^*} \; . \tag{4.19}$$

Rewrite eq. (4.18) as

$$E_+ - E_- = D[(\phi_+^{*\,2/\rho} - \phi_-^{*\,2/\rho}) - 2(\phi_+^{*\,1/\rho} - \phi_-^{*\,1/\rho})] + c(Q_+^* - Q_-^*)p. \tag{4.20}$$

Then

$$(E_+ - E_-)' = 2D\rho^{-1}\,[(\phi_+^{*\,2/\rho-1}\phi_+^{*\prime} - \phi_-^{*\,2/\rho-1}\phi_-^{*\prime}) - (\phi_+^{*\,1/\rho-1}\phi_+^{*\prime} - \phi_-^{*\,1/\rho-1}\phi_-^{*\prime})] + c(Q_+^* - Q_-^*) + c(Q_+^{*\prime} - Q_-^{*\prime})p. \tag{4.21}$$

The energy at the terminal points of oscillation in the excited state is

$$RD(1 - \gamma\phi^*_\pm)^2 + rcQ^*_\pm p + E_0 = V^*_m + kT/2. \tag{4.22}$$

Defining $\alpha^* = \sqrt{kT/2RD}$ and recalling eq. (2.17), we have

$$1 - \gamma\phi^*_\pm(0) = \pm\,\alpha^* \tag{4.23}$$

or

$$\phi^*_\pm(0) = (1 \mp \alpha^*)/\gamma \tag{4.24}$$

and

$$Q^*_\pm(0) = q - \frac{\log(1 \mp \alpha^*)}{\rho\beta} \quad . \tag{4.25}$$

Furthermore,

$$\phi^{*\prime}_\pm = -\rho\beta Q^{*\prime}_\pm e^{-\rho\beta Q^*_\pm} \tag{4.26}$$

and

$$-2RD\gamma\phi^{*\prime}_\pm(1 - \gamma\phi^*_\pm) + rc(Q^{*\prime}_\pm p + Q^*_\pm) = V^{*\prime}_m , \tag{4.27}$$

whence with eq. (2.18)

$$\phi^{*\prime}_\pm(0) = \mp \frac{rc \log(1 \mp \alpha^*)}{2R\rho\beta D\alpha^*\gamma} \tag{4.28}$$

and

$$Q^{*\prime}_\pm(0) = \mp \frac{rc \log(1 \mp \alpha^*)}{2R\rho^2\beta^2 D\alpha^*(1 \mp \alpha^*)} \quad . \tag{4.29}$$

Applying Maclaurin series as before, we have

$$\begin{aligned} E_+ - E_- &= (E_+ - E_-)_0 + (E_+ - E_-)'_0 p \\ &\cong \frac{D^*_\alpha(\gamma^{1/\rho} - 1)}{\rho\gamma^{2/\rho}} + \frac{c^*\alpha}{\rho\beta}\left\{\frac{r\,(2-2\rho)\gamma^{1/\rho} - (4-3\rho)}{R\rho\gamma^{2/\rho}} + 2\right\}p \end{aligned} \tag{4.30}$$

and the Gaussian half-width,

$$\varepsilon_e = r(kTD \log 2)^{\frac{1}{2}}(\gamma^{1/\rho}-1)/\rho\gamma^{2/\rho}\sqrt{R}$$

$$+ \frac{c}{\rho\beta}\left(\frac{kT \log 2}{RD}\right)^{\frac{1}{2}}\left\{\frac{r[(2-2\rho)\gamma^{1/\rho}-(4-3\rho)]}{R\rho\gamma^{2/\rho}} + 2\right\}p \quad . \tag{4.31}$$

V. PANSYNTHESIS

It remains to cast the model in a form convenient for application to experimental data. Following the procedure adopted in Reference 1, we square eqs. (4.17) and (4.31) and subtract the terms independent of pressure to obtain

$$\begin{aligned} \delta\varepsilon_a^2/N^2 &= (c/\beta)R\gamma\rho(1-\gamma)\ \{R\gamma\rho[2\rho-3-\gamma(4\rho-3)] + 2r\}p \\ &\quad + (c^2/8\beta^2 D)\{R\gamma\rho[2\rho-3-\gamma(4\rho-3)] + 2r\}^2 p^2 \end{aligned} \tag{5.1}$$

and

$$\begin{aligned} \delta\varepsilon_e^2/N^2 &= (c/R\rho^2\beta\gamma^{2/\rho})\{r[(2-2\rho)\gamma^{1/\rho}-(4-3\rho)]/R\rho\gamma^{2/\rho} + 2\}p \\ &\quad + (c^2/8RD\rho^2\beta^2)\{r[(2-2\rho)\gamma^{1/\rho}-(4-3\rho)]/R\rho\gamma^{2/\rho} + 2\}^2 p^2, \end{aligned} \tag{5.2}$$

where, as in Ref. 1, $N = (8kT \log 2)^{\frac{1}{2}}$.

Spectroscopic measurements such as those of References 6 and 7 can be expressed in the form

$$\delta\mathcal{E}_a = a_1 p + a_2 p^2, \tag{5.3}$$

$$\delta\mathcal{E}_e = e_1 p + e_2 p^2, \tag{5.4}$$

$$\delta\varepsilon_a = d_a p, \tag{5.5}$$

and

$$\delta\varepsilon_e = d_e p, \tag{5.6}$$

where the coefficients on the right are empirical fitting parameters.

As was pointed out in Ref. 1, we can write

$$\delta\varepsilon_a^2/N^2 = 2E_a p + D_a p^2 \tag{5.7}$$

and

$$\delta\varepsilon_e^2/N^2 = 2E_e p + D_e p^2 \ , \tag{5.8}$$

where $E_a = d_a\varepsilon_a^o/N^2$, $D_a = d_a^2/N^2$, ε_a^o is the absorption half-width at zero pressure, etc.

Equations (5.1) - (5.8) with eqs. (3.3) and (3.6) give us finally, defining $\bar{\beta} = \beta/c$,

$$a_1 = R\rho\gamma(\gamma - 1)/\bar{\beta} \ , \tag{5.9}$$

$$a_2 = \{R\rho\gamma[\rho(2\gamma-1) - 3(\gamma-2)] + (1-2r)\}/4\bar{\beta}^2 D, \tag{5.10}$$

$$E_a = R\rho\gamma(1-\gamma)\{R\rho\gamma[2\rho-3-\gamma(4\rho-3)] + 2r\}/2\bar{\beta}, \tag{5.11}$$

$$D_a = \{R\rho\gamma[2\rho-3-\gamma(4\rho- 3)] + 2r\}^2/8\bar{\beta}^2 D, \tag{5.12}$$

$$e_1 = r\gamma^{-1/\rho}(1-\gamma^{-1/\rho})/R\rho^2\bar{\beta} + q(r-1), \tag{5.13}$$

$$e_2 = r\gamma^{-1/\rho}\{r[(1-2\gamma^{-1/\rho}-3\rho(1-\gamma^{-1/\rho})] + R(2-r)\}/4R^2\rho^2\ \bar{\beta}^2 D, \tag{5.14}$$

$$E_e = \{r[(2-2\rho)\gamma^{1/\rho}-(4-3\rho)]/R\rho\gamma^{2/\rho} + 2\}/2R\rho^2\bar{\beta}\gamma^{2/\rho}, \tag{5.15}$$

$$D_e = \{r[(2-2\rho)\gamma^{1/\rho}-(4-3\rho)]/R\rho\gamma^{2/\rho} + 2\}^2/8RD\rho^2\bar{\beta}^2 \ . \tag{5.16}$$

VI. CONCLUDING REMARKS

Proceeding in the spirit of Drickamer et al[2,3,4], we have derived from a Morse potential a set of equations for evaluating the configuration-coordinate parameters that describe the effects of high pressure on optical absorption and emission spectra. These eight equations relate seven unknown parameters ($\bar{\beta}$, D, q, R, r, ρ) to eight experimentally accessible quantities. We have made the following assumptions:

1. The pressure dependence of peak height is second order, and that of bandwidth first order.

2. The constants in the Morse function, β and D, are independent of pressure.

3. The parameters can be regarded as averages over all normal modes and configuration coordinates.

The first assumption is consistent with experimental evidence[6,7]. The second assumption is suggested by Lin's[5] conclusions from first-order perturbation theory in the harmonic approximation. The third assumption is necessary to avoid an intractable proliferation of parameters. If future experimental results should force a relaxation of the first assumption, it is necessary only to carry the Maclaurin expansions to higher order.

Resources are not at present available to exercise eqs. (5.9) - (5.16) on the experimental data. It might even be questioned whether such an endeavor is worthwhile until more data are at hand. In principle the Morse potential should be more accurate than the harmonic oscillator. It would be desirable to have a perturbation treatment similar to that applied by Lin[5] for the harmonic oscillator.

The significant work by Berry and Williams[8] and Curie and Williams[9] in deriving a model of pressure effects from first principles has come to my attention since completing the work presented here. Although their model in its harmonic approximation works well for inorganic crystals, it is, like the original Drickamer model, qualitatively inconsistent with experiments on aromatics. However, a Morse treatment of that model along the lines of the present paper may bear fruit.

Reference 1a details the motivation of this work from an interest in pressure effects on burning rates of propellants. It has now become clear that the effects under study are unlikely to change dissociation energy sufficiently to influence reaction rates. Since this approach to propellant phenomenology no longer appears promising, the work has been discontinued.

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8. Berry, D., and Williams, F., Acta Physica Polomica A54, 705 (1978).
9. Curie, D. and Williams, F., in Luminescence of Inorganic Solids, B. Di Bartolo ed., New York: Plenum Press (1978).

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REFERENCES

1. Tompkins, R.C., J. Chem. Phys. 69, 579 (1978).

2. Drickamer, H.G., Frank, C.W., and Slichter, C.P., Proc. Nat. Acad. Sci. (USA) 69, 933 (1972).

3. Drickamer, H.G., and Frank, C.W., "Electronic Transitions and the High Pressure Chemistry and Physics of Solids, "London: Chapman and Hall (1943).

4. Okamoto, B.Y., Drotning, W.E., and Drickamer, H.G., Proc. Nat. Acad. Sci. (USA) 71, 2671 (1973).

5. Lin, S.H., J. Chem. Phys, 59, 4458 (1973).

6. Okamoto, B.Y., and Drickamer, H.G., J. Chem. Phys., 61, 2870 (1974).

7. Okamoto, B.Y., and Drickamer, H.G., J. Chem. Phys., 61, 2878 (1974).

8. Berry, D., and Williams, F., Acta Physica Polomica A54, 705 (1978).

9. Curie, D. and Williams, F., in Luminescence of Inorganic Solids, B. Di Bartolo ed., New York: Plenum Press (1978).

APPENDIX

This appendix gives the requisite expansions in Maclaurin series.

$$\sqrt{1+2cp/\beta D} = 1 + cp/\beta D - c^2p^2/2\beta^2D^2 + \ldots \tag{A.1}$$

$$\log(1 + \sqrt{1+2cp/\beta D}) = \log 2 + cp/2\beta D - 3c^2p^2/4\beta^2D^2 + \ldots \tag{A.2}$$

$$[(1 + \sqrt{1+2cp/\beta D})/2]^{\rho} = a + \rho cp/2\beta D + \rho(\rho-3)c^2p^2/8\beta^2D^2 + \ldots \tag{A.3}$$

$$\sqrt{1+2rcp/R\rho\beta D} = 1 + rcp/R\rho\beta D - r^2c^2p^2/2R^2\rho^2\beta^2D^2 + \ldots \tag{A.4}$$

$$\log(1 + \sqrt{1+2rcp/R\rho\beta D}) = \log 2 + rcp/2R\rho\beta D - 3r^2c^2p^2/4R^2\rho^2\beta^2D^2 + \ldots \tag{A.5}$$

$$\begin{aligned}[(1 + \sqrt{1+2rcp/R\rho\beta D})/2]^{1/\rho} &= 1 + rcp/2R\rho^2\beta D \\ &\quad + r^2c^2(1-3\rho)p^2/8R^2\rho^4\beta^2D^2 + \ldots\end{aligned} \tag{A.6}$$

$$\log(1 \pm \alpha) = \pm\alpha - \tfrac{1}{2}\alpha^2 \pm (1/3)\alpha^3 - \ldots \tag{A.7}$$

$$(1 \pm \alpha)^{\sigma} = 1 \pm \sigma\alpha + \tfrac{1}{2}\sigma(\sigma-1)\alpha^2 \pm [\sigma(\sigma-1)(\sigma-2)]\alpha^3/6 + \ldots \tag{A.8}$$

$$(1 \pm \alpha)^{\sigma}\log(1 \pm\alpha) = \pm\alpha + \tfrac{1}{2}(2\sigma-1)\alpha^2 \pm [3\sigma(\sigma-2) + 2]\alpha^3/6 + \ldots \tag{A.9}$$

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