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Dissociation Energy and Long-Range Potential of Diatomic Molecules From Vibrational Spacings: The Halogens

by

Robert J. Le Roy and Richard B. Bernstein

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(i) Page 25. In Table V the v_H values for the two bromine isotopes should be 53 (not 50).

(ii) Page 61, ℓ. 2-3 should read:

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C*** FIT POLYNOMIALS OF INCREASING ORDER TO THE DATA TILL THE
C    DECREASE IN THE SUM OF SQUARES OF RESIDUALS DUE TO THE
C    HIGHEST POWER TERM IS NOT STATISTICALLY SIGNIFICANT
C    (ACCORDING TO A PARTIAL F-TEST), OR THE STANDARD ERROR
C    BECOMES LESS THAN  ERY.
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(iii) Pages 67 and 79. The three cards immediately following statement number 1000 should be removed and this section should read:

```
1000 A(KK) = 1.DO/AMAX
     NK = N*NDIM
     DO 1500  I = 1,N
     NK = NK-NDIM
     K = N-I+1
     IF (ROW(K) .EQ. K) GO TO 1500
```

All results reported are unaffected by these errors.

June 29, 1970

Dissociation Energy and Long-Range Potential of Diatomic Molecules From Vibrational Spacings: The Halogens[*]

by

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Abstract

A recently developed method for obtaining dissociation limits and long-range internuclear potentials from the distribution of the uppermost vibrational levels of diatomic molecules is applied to existing data for the B $^3\Pi^+_{0u}$ states of $C\ell_2$, Br_2 and I_2, and the ground $X^1\Sigma^+_g$ state of $C\ell_2$. Values of the asymptotic long-range potential constants (C_n) are deduced from the data; they compare well with the best theoretical estimates. The analysis yields improved D_o values for the ground $X^1\Sigma^+_g$ states of $^{35,35}C\ell_2$, $^{79,79}Br_2$, $^{81,81}Br_2$ and $^{127,127}I_2$, respectively as follows: $19997.2_5(\pm0.3)$, $15894.5(\pm0.4)$, $15896.6(\pm0.5)$, and $12440.9(\pm1.2)$ cm^{-1}. Presented also are: (1) a convenient graphical approximation procedure for utilizing the method, and (2) a graphical means of making vibrational assignments for higher levels when gaps exist in the observed vibrational sequence. The latter approach suggests certain vibrational reassignments for ground-state $C\ell_2(X^1\Sigma^+_g)$ and for Br_2 (B $^3\Pi^+_{0u}$).

I. Introduction

An expression has recently been derived which relates the distribution of vibrational levels near the dissociation limit D of a diatomic molecule to the attractive long-range part of its internuclear potential (1,2). For the common situation where the outer branch of the potential may be closely approximated by the attractive inverse-power functionality:

$$V(R) = D - C_n/R^n \quad , \tag{1}$$

the distribution of vibrational eigenvalues $E(v)$ near D is closely approximated by

$$\frac{d}{dv}\left[E(v)\right] = K_n\,[D-E(v)]^{\left(\frac{n+2}{2n}\right)} . \tag{2}$$

Using physical constants from Ref. (3), the constant K_n is

$$K_n = \left[\frac{14.55487}{(\mu)^{1/2}(C_n)^{1/n}}\right]\left[\frac{n\,\Gamma(1+\frac{1}{n})}{\Gamma(\frac{1}{2}+\frac{1}{n})}\right] \tag{3}$$

for D and $E(v)$ in cm^{-1}, the reduced mass μ in amu, and C_n in $cm^{-1}\text{Å}^n$. As usual, $\Gamma(x)$ is the gamma function (4). A more useful expression is obtained by integrating Eq. (2):[1]

$$E(v) = D - [(v_D - v)H_n]^{\left(\frac{2n}{n-2}\right)} , \qquad n \neq 2, \tag{4}$$

where $H_n = (\frac{n-2}{2n})K_n$, and for $n>2$ the integration constant v_D is the "effective" vibrational index at the dissociation limit, $E(v_D) = D$. Truncating v_D to an integer then yields the vibrational index of the highest bound rotationless level supported by the potential. Consideration of the third derivative of Eq. (4) shows that Birge-Sponer plots should show positive (upward) curvature for levels lying close to D where Eq. (1) is appropriate. The significance of the parameters and the types of errors inherent in Eqs. (1)-(4) are discussed in Ref. (2).

In general, values of the four unknowns D, n, C_n and v_D may be obtained from a least-squares fit of experimental vibrational energies to Eq. (4). However, since it is non-linear in the parameters, Eq. (4) require good initial trial parameter values if the fit is to converge uniquely. All of the results presented below were obtained from general fits to Eq. (4), using initial trial values obtained by the method presented in Refs. (2) and (5). Computer programs for these regression procedures are listed in Ref. (5).

The general smoothing and regressions techniques discussed in Refs. (2) and (5) yield the best parameter values obtainable from Eqs. (2-4). However, results with almost the same accuracy may be obtained from a simple graphical treatment of the data, described below, if two extra conditions are satisfied. First, the value of $\tilde{n}$, the asymptotic value of the power in Eq. (1), must be known.[2] Second, the levels must be sufficiently "dense" to allow use of the approximation

$$\frac{dE(v)}{dv} \simeq \overline{\Delta G}_v \equiv \frac{1}{2}[\Delta G_{v-\frac{1}{2}} + \Delta G_{v+\frac{1}{2}}] = \frac{1}{2}[E(v+1) - E(v-1)] \quad , \qquad (5)$$

Then, with n held fixed at $\tilde{n}$,[2] Eq. (2) yields the approximate expressions

$$(\overline{\Delta G}_v)^{(\frac{2n}{n+2})} = [D-E(v)]\ (K_n)^{(\frac{2n}{n+2})} \quad , \tag{6}$$

suggesting a plot of $(\overline{\Delta G}_v)^{(\frac{2n}{n+2})}$ vs. $E(v)$. For the highest levels this should be linear with intercept D, while for the relatively deeper levels it should show negative curvature. Hence, a linear extrapolation from such a plot should always give an upper bound to D. Once D has been determined in this manner, Eq. (4) may be rewritten as

$$[D-E(v)]^{(\frac{n-2}{2n})} = (v_D-v)H_n \tag{7}$$

With $n=\tilde{n}$, a plot of the left hand side vs. v yields v_D as the intercept, and H_n (and hence C_n) from the slope. The usefulness of Eqs. (5-7) is demonstrated below.

In Sec. II, Eq. (4) is fitted to the experimental vibrational energies of the B $^3\Pi^+_{0u}$ states of $C\ell_2$, Br_2 and I_2, yielding estimates of the asymptotic long-range potential constants, C_5, and improved values of the ground-state dissociation energies.[3] A further application of Eq. (4) is introduced in Sec. III, which suggests vibrational reassignments for the highest observed levels of Br_2 (B $^3\Pi^+_{0u}$) and of ground state $C\ell_2(X^1\Sigma_g^+)$. In the latter case, a fit to Eq. (4) then yields estimates of v_D and of the long-range C_6 constant.

II. Ground State Dissociation Energies and B $^3\Pi^+_{0u}$ State Potential Tails of the Halogens

A: Chlorine[4]

A detailed discussion of the fitting of the experimental data of Douglas et al (9) for $C\ell_2$ (B $^3\Pi^+_{0u}$) to Eq. (4) has been presented (2). However, the reported (1,2) uncertainties in the parameters were incorrectly described as 95% statistical confidence intervals; they were actually two standard deviations, corresponding to the 95% confidence level only in the limit of many degrees of freedom. Parameter values obtained on fitting the experimental energies (9) to Eq. (4) with n free or fixed at $\tilde{n}=5$[2] are given in Fig. 1, together with the proper 95% confidence intervals[5].

As was concluded in Ref. (2), the highest observed levels of $C\ell_2$ (B $^3\Pi^+_{0u}$) depend mainly on the theoretical asymptotic $\tilde{n}=5$ inverse-power term in the long-range potential.[2] The disagreement with the $\tilde{n}=6$ suggestion of Byrne, Richards, and Horsley (10) is discussed in Sec. IV. The values of D, C_5, and v_D reported in Ref. (2) (which also gave predicted energies of the unobserved highest bound levels of this state) are listed for the sake of completeness in Table I, together with the improved estimates of their uncertainties.[6] Similarly included are the results for the other halogen systems, to be discussed below.[7]

While the parameters given in Table I are the best values obtainable from the available experimental data (9) using the present method, results of nearly the same quality are obtained on utilizing these data (9) directly in the simple graphical manner suggested by Eqs. (5-7). For this case the theoretical $\tilde{n}=5$,[2] and Fig. 2 shows the plot suggested by Eq. (6); the intercept is indistinguishable from the value of D obtained from the fits to Eq. (4) (see Table I). Using this D and $n=\tilde{n}=5$, Fig. 3 shows the plot suggested by Eq. (7); its slope and intercept are very close to the fitted values of H_n and v_D.

Combining the fitted D value for $C\ell_2$ $(B\ {}^3\Pi^+_{ou})$ with the ${}^2P_{1/2} - {}^2P_{3/2}$ atomic $C\ell$ spin-orbit splitting of 882.50 cm^{-1} (12,13) yields a ground state dissociation energy of $D_o = 19997.25\ (\pm 0.3)$ cm^{-1}. This differs significantly from both the estimate of $D_o = 20062(\pm 40)$ cm^{-1} obtained by Rao and Venkateswarlu (14) from a Birge-Sponer extrapolation of their ground-state vibrational data, and from the $D_o = 20040(\pm 20)$ cm^{-1} which Clyne and Coxon (15) obtained on reinterpreting their data (14). However, the discrepancy is removed by the vibrational reassignment of the highest observed ground-state level, discussed below in Sec. III.

B: Bromine

The present analysis of the $B\ {}^3\Pi^+_{0u}$ state of Br_2 makes use of concurrent fitting to Eq. (4) of data for different isotopes in a given molecular electronic state. The only assumption required is that the long-range potential tails of the isotopic species be identical.[8] If the isotopic potentials are assumed to be identical everywhere, the number of free parameters in the problem is reduced further, since the ratio of v_D values for isotopic species i and j is then determined solely by the reduced mass ratio:

$$v_D(j)/v_D(i) = [\mu(j)/\mu(i)]^{1/2} \quad . \tag{8}$$

To obtain trial parameter values for a multi-isotope case (5), Eq. (8) is assumed and the relative isotope shifts are estimated.[9] (Alternately, trial parameter values may be estimated separately by applying Eqs. (5-7) or the method of Ref. (2) to the data for the individual isotopic molecules.) However, in the final fits to Eq. (4), D, n, C_n, v_D for each isotope, and the relative energy shifts (ground-state zero-point energy shifts[3]) for the different species were allowed to be free parameters.

Horsley and Barrow (18) have measured vibrational energies of four adjacent vibrational levels, v=50-53, near the dissociation limits of the B $^3\Pi^+_{0u}$ states of $^{79,79}Br_2$ and $^{81,81}Br_2$. (It is suggested in Sec. III that their vibrational assignment for these levels is one unit too small; the new numbering is used here.) Unfortunately, a fit of these eight observations to Eq. (4) with all six parameters free did not yield a reliable value of $\tilde{n}$. However, since all the levels considered lie within 20 cm^{-1} of the dissociation limit, it is probable that they depend primarily on the theoretical[2] asymptotic potential behavior ($V(R) \sim R^{-5}$). The plausibility of this assumption is strengthened by consideration of Fig. 2 which shows that for $C\ell_2$ (B $^3\Pi^+_{0u}$), the levels within ca. 40 cm^{-1} of D accord with $\tilde{n} = 5$, while the theoretical C_5 for $C\ell_2$ is considerably smaller than that for Br_2.[10]

Fixing $n=\tilde{n}=5$,[2] the eight data were fitted to Eq. (4), yielding the parameters given in Table I, and an isotopic zero point energy shift of 2.05 (± 0.12) cm^{-1}.[5] The latter is in good agreement with the more precise value of 2.029 (± 0.014) cm^{-1}, the difference between the ground-state isotopic zero point energies calculated from the vibrational constants of Ref. (18).

The ratio of the Br_2 isotopic v_D's in Table I agrees well within the uncertainty of the fit with that predicted by Eq. (8), confirming its validity for this case. Hence, Eq. (8) may be applied to the mixed isotopic molecule $^{79,81}Br_2$, yielding $v_D = 60.89$. Furthermore, the (79,79)-(81,81) isotope shift suggests a value of $D = 19580.7_4$ cm^{-1} for the mixed isotope (79,81). Using these interpolated parameters and the constants given in Table I, the energies of the highest vibrational levels of the $B\ ^3\Pi^+_{0u}$ potential may be predicted from Eq. (4) for all three isotopic species. In Table II these are compared to the experimental energies of Ref. (18) for the pure (79,79) and (81,81) isotopes, and of Brown (20) for (79,81).[11]

As in the discussion of $C\ell_2$, it is interesting to compare the best fitted parameter values with the estimates of them which would have been obtained from Eqs. (5-7), with $n=\tilde{n}=5$.[2] In this case the two isotopes must be considered separately; for each, the four observed energies yield only two $\overline{\Delta G}_v$ values which uniquely determine the intercepts D. These resultant D values for (79,79) and (81,81) are respectively only 0.05 cm^{-1} and 0.15 cm^{-1} larger than the best fitted values (Table I). Using these (approximate) D's and fixing $n=5$, Eq. (7) then yields Fig. 4. As before (for $C\ell_2$, see Fig. 3) the slopes and intercepts lie within the statistical uncertainties in the fitted Table I parameter values.

Combining the fitted D values for the pure isotopes with the 3685.2(±0.3) cm^{-1} spin-orbit splitting (21) yields ground state dissociation energies of D_o (79,79) = 15894.5(±0.4) cm^{-1}, and D_o (81,81) = 15896.6(±0.5) cm^{-1}. The consistent estimated value for the mixed isotope is D_o (79,81) = 15895.5(±0.5) cm^{-1}.

C: Iodine[12]

The only quantitative data for this state extending above v=58 appear to be Brown's (22) band-head measurements for levels v=48 to 72.[13] Since a Birge-Sponer plot of his vibrational spacings shows positive curvature everywhere, these data are suitable for treatment by the present method.

As for $C\ell_2$ (B ${}^3\Pi^+_{0u}$) (2), the vibrational energies were repeatedly fitted to Eq. (4) while the deeper levels were successively omitted from consideration. This was done in turn with all four parameters being varied freely, and with n fixed at $\tilde{n}$=5. The resulting parameter values are shown in Fig. 5, plotted against the energy of the lowest level included in a given fit, $E(v_L)$.[5] Unfortunately, the scatter in the data is such that the four-parameter fits become unstable when fewer than 10 levels are considered at once, precluding a direct determination of $\tilde{n}$. Even when n is held fixed at $\tilde{n}$=5, the three-parameter fits become erratic when fewer than 9 levels are considered at once.

While reliable "local values" of n cannot be determined directly, the flattening of the three dashed curves in Fig. 5 for $v_L \gtrsim 55$ strongly suggests that the highest *ca.* 18 observed levels lie in the asymptotic ($\tilde{n}=5$) region. This is qualitatively confirmed by the fact that the fitted C_5 values are within 30% of the theoretical value[10] of $4.5_4 \times 10^5$ cm^{-1} Å^5. The present best estimates of D, C_5, and v_D, presented in Table I, were obtained by weighting the results for $v_L=55$ to 64 by the squared inverse of their uncertainties.[7] This v_D suggests that this state has 15 vibrational levels above the highest one observed by Brown (22); predicted values of their energies, generated from Eq. (4) and the parameters in Table I, are given in Table III.

As in the previous cases, the best fitted parameter values can be compared to estimates of them obtainable from Eqs. (5-7). Fig. 6, based on Eqs. (5-6), yields an estimate of D indistinguishable from the value in Table I. Furthermore, the linearity of this plot for $v \gtrsim 55$ confirms the dominant $\tilde{n}=5$ influence in this region. The ensuing plot based on Eq. 7 (Fig. 7) yields estimates of v_D and H_n lying well within the statistical uncertainties in the Table I values.

Combining the fitted value of D with the 7603.15 cm^{-1} atomic $^2P_{1/2} - {}^2P_{3/2}$ splitting (12,25) yields a ground-state dissociation energy of $D_o = 12440.9(\pm1.2)$ cm^{-1}.[7] The source of the disagreement between this result and Verma's (26) $D_o = 12452.5(\pm1.5)$ cm^{-1} is discussed elsewhere (11).

III. Proposed Vibrational Reassignments

A. General

Frequently the energies and indexing of the deeper vibrational levels of a given electronic state are accurately known, while near its dissociation limit D the data are often relatively sparse, with gaps of several vibrational quantum numbers between observed levels. In the absence of additional information, this may lead to errors in vibrational assignments.

One constraint which may be applied to the data is to require that the Birge-Sponer plot for the species in question should have positive curvature for levels near D (1,2). The present approach implicitly includes this constraint while making more explicit use of Eq. (4). The necessary assumptions are a value for $\tilde{n}$, and a good estimate of D which is independent of the vibrational numbering under dispute. Then, (according to Eq. (7)), for n fixed at $\tilde{n}$, a plot of $[D-E(v)]^{(\frac{n-2}{2n})}$ vs v should be linear for levels very near D, while showing progressively stronger negative curvature for deeper levels (see discussion in Sec. I). Since the long-range interatomic interaction may be expressed (27,28) as a sum of inverse (integer)-power terms in R (of lowest order $\tilde{n}$), the effective "local" n at the outer turning points increases with the binding energy. However, consideration of Eq. (4) shows that in the limit of very large n, $[D-E(v)]$ varies directly as $(v_D-v)^2$. Thus, a plot of $[D-E(v)]^{\frac{1}{2}}$ vs. v should have strong positive curvature near the dissociation limit (for $\tilde{n} > 4$ this curvature becomes infinite at D), while becoming increasingly linear for the deeper levels.

The present approach consists of requiring the vibrational assignment to be such that the two types of plot discussed above show the appropriate curved and linear regions. As a check, in Fig. 8 this approach was applied to the data of Douglas et al (9) for $C\ell_2$ ($B\ ^3\Pi^+_{0u}$), for which $\tilde{n}$=5.[2] Clearly, even had there been a gap of 10 unobserved levels somewhere in the range, Fig. 8 would have unambiguously fixed the vibrational assignments.

B: Vibrational Reassignment and Potential Tail of Ground-State $C\ell_2(X\,^1\Sigma^+_g)$

The only experimental data for highly excited vibrational levels of ground state $C\ell_2$ are the UV resonance emission doublets reported by Rao and Venkateswarlu (14). The rotational assignment for these doublets has recently been revised (15) yielding slightly different energies, and these are used here. However, the validity of the present discussion does not hinge on this change.

In Ref. (14) the extrapolation of a Birge-Sponer plot gave a value for the ground state dissociation energy 65(±10) cm^{-1} larger than that of Sec. IIA.[14] Furthermore, this plot showed growing negative curvature near the dissociation limit, which would be worsened if the extrapolation were constrained to yield the present D_o. This is the opposite of the expected behavior in this region, especially since the vibrational spacings for the analogous (but shallower) ground electronic state of I_2 (29) show positive curvature for levels lying within 1000 cm^{-1} of the dissociation limit. Although one expects the long-range inverse-power attractive potential tail to be somewhat weaker for $C\ell_2$ than for I_2, its influence on the highest vibrational levels should not disappear altogether.

Ref. (14) reported observations of all adjacent or semi-adjacent ground-state levels from $v=9$ to 42. Above this point four other levels were observed, separated by gaps assigned respectively as two, three, two, and one unobserved levels. The anomalous increasingly negative Birge-Sponer curvature is explained if these gaps are too small. Using the theoretical $\tilde{n}=6$[2] and the ground-state dissociation energy obtained in Sec. II A, the observed levels (re-evaluated using the rotational reassignment of Ref. (15)) are presented in Fig. 9 in the form suggested by the preceding section. Above $v=42$, each pair of adjacent points is joined by a straight line which is extrapolated to the tie line corresponding to the next higher observed level. The possible vibrational assignments correspond to integer values of v on these tie lines, and the three pairs of curves in Fig. 9, (A,A'), (B,B') and (C,C') correspond to the only plausible sets of assignments.

In Fig. 9, curves (C,C') correspond to the original assignment (14); as stated above and confirmed by the curvature shown, this is implausible. Curve A shows positive curvature for the higher levels which is too pronounced to be due to experimental error. However, the slight positive curvature in B at the highest observed level is within the uncertainty in the experimental energies.[15] Thus, it appears that the (B,B') reassignment of the original (14) $v=54$ as $v=55$ is correct.

The main restriction on the use of this approach is the requirement for a good initial value of D. Applying the method to the same energies using trial D values in turn 50 cm^{-1} smaller and larger than the present value would have yielded (C,C') and (A,A') respectively as the most probable assignments. On the other hand, using D_o = 20012 cm^{-1}, the best estimate available previous to Ref. (<u>14</u>), the present reassignment is obtained.

It is important to note that this reassignment negates the speculation concerning a possible barrier maximum (<u>9</u>,<u>15</u>). No such maximum is expected theoretically, since for the ground states of the halogens, at least the first two non-zero inverse-power potential terms are attractive (see the argument presented for I_2 in Ref. (<u>11</u>)), as well as the exchange forces which give rise to the chemical binding.

Using the known $\tilde{n}$=6 and D_o for the ground state, Eq. (4) was fitted to the three highest experimental energies (v=49, 52 and 55) yielding the values of C_6 and v_D given in Table I. The C_6 obtained is in fortuitously good agreement with the theoretical $C_6 = 0.82 \times 10^5 \ cm^{-1} \ \mathring{A}^6$, estimated by Caldow and Coulson (<u>30</u>). However, fitting the highest two levels using the (A,A') and (C,C') vibrational assignments would yield C_6 values respectively 7 times larger and 1/8 as large as the theoretical estimate. This lends credence to both the present vibrational reassignment and the significance of the fit itself. Table IV presents the energies predicted by the constants in Table I for the highest bound levels of $C\ell_2$ $(X^1\Sigma_g^+)$. 15

C: Vibrational Reassignment for Br_2 ($B\ ^3\Pi^+_{0u}$)

The four vibrational levels observed near the dissociation limit of the $B\ ^3\Pi^+_{0u}$ state of each of $^{79,79}Br_2$ and $^{81,81}Br_2$ were originally assigned as v=49-52 (18). The only other measurements of the upper vibrational levels of this state are Brown's (20) observation of levels up to v=48 of $^{79,81}Br_2$. In order to compare these results, the (79,79) and (81,81) energies (18) were averaged to yield approximate (79,81) energies for the levels considered. For this species ($\tilde{n}=5$ $\overset{2}{\vee}$ and D was obtained in Sec. II B), Fig. 10 is the plot suggested by Sec. IIIA. The solid points are from Ref. (20) and the open points are the interpolated energies mentioned above. It is apparent that the original (18) vibrational numbering of the latter four levels must be increased by one. This reassignment was used in Sec. II B.

IV. Discussion

A: Comparison of $B\ ^3\Pi^+_{0u}$ State D Values with Previous Results

Most of the results in Table I differ somewhat from previous dissociation limits and conclusions about the nature of the long-range potentials, despite being based on the same data. For the D values, the appropriate quantity for comparison is $[D-E(v_H)]$, the binding energy of the highest observed level. Table V compares the present and best previous values of this quantity for the $B\ ^3\Pi^+_{0u}$ states of the halogens.

In the case of I_2 the discrepancy originates in the graphical extrapolation of Ref. (22) beyond the highest observed levels. This illustrates the errors which may arise from use of the Birge-Sponer (31) and Birge (32) extrapolation procedures.[16]

The previous best estimates of the dissociation limits of the (79,79) and (81,81) isotopes of Br_2 $(B\ {}^3\Pi^+_{0u})$ (18) were based on limiting curves of dissociation (e.g., see Chapt. VI of Ref. (33)). The discrepancy with the present results implies that the absorption series were incomplete; i.e., they did not extend to the predissociation limit. It has been shown (34) that for vibrational levels lying near the dissociation limit, the energies at which the rotational series for the different vibrational levels break off due to predissociation should vary as $[J_m(J_m+1)]^{\left(\frac{n}{n-2}\right)}$, where $n=\tilde{n}$, and J_m is the rotational quantum number of the last unpredissociated level. For Br_2 $(B\ {}^3\Pi^+_{0u})$, (for which $\tilde{n}=5$[2]) the theoretical C_5 coefficient[10] yields a predicted slope of $2.0\text{x}10^{-5}[\text{cm}^{-1}]$ for plots of $E(J_m)$ vs $[J_m(J_m+1)]^{5/3}$. Since the data (18) do not conform to this behavior, it is inferred that the experimenters did not observe the very highest non-predissociating levels. This is consistent with their lack of observation of any broadened lines.

One further effect to be considered is the effect on the fitted D value of an error in the chosen value of $\tilde{n}$. Fitting the data to Eq. (4) in the manner described in Sec. II, but with n set equal to 6 instead of 5, one obtains D values for $C\ell_2$, Br_2, and I_2, respectively which are only 0.36, 0.50 and 2.7 cm^{-1} smaller than the best values (Table I).

B: The B $^{3}\Pi^{+}_{0u}$ State Potential Tails. Comparison with Previous Results and with Theory

Byrne et al (10) concluded that the outer RKR turning points (35) for the B $^{3}\Pi^{+}_{0u}$ states of both $C\ell_2$ and Br_2 followed an R^{-6} dependence, rather than the theoretical[2] asymptotic R^{-5} form. However, the validity of this conclusion is contingent on the accuracy of the RKR potential and of the value of D assumed.

For $C\ell_2$ the reported turning points (35) are plotted against binding energy in Fig. 11, using both the present D and the experimenters' (9) D (presumably the value used in Ref. (10)).[17] The small difference between these D's has a negligible effect on this plot, and it appears that the previous $\tilde{n}=6$ deduction is wrong since it requires ignoring the last few levels. (This also implies that the reported (10) "C_6" is spurious.) The difference between the intercepts of curves A and B in Fig. 11 indicates that either the present best C_5 is ca. 40% small, or that the RKR results are slightly in error. The latter is plausible since no experimental data were available for the lowest six levels of this state, spanning the lower 40% of the potential well.

The RKR potential for Br_2 (B $^{3}\Pi^{+}_{0u}$) from which Byrne et al (10) concluded $\tilde{n}=6$ appears to have been calculated (35) for the mixed isotope (79,81) from the averaged Ref. (18) data for (79,79) and (81,81). However, these results only span levels $9 \leq v \leq 19$ and $50 \leq v \leq 53$, and $v=9$ lies ca. 37% of the well depth above the minimum. In addition to using the incorrect original (18) vibrational assignment for the four high levels ($49 \leq v \leq 52$), the interpolation over the large gaps in the spectrum is quite unreliable. For example, the interpolated $v=30$ and 45 (79,81) energies are respectively 6 and 9 cm^{-1} higher than the values reported by Brown (20), while the extrapolated (35) [E(9)-E(0)] is 8 cm^{-1} larger than the value obtained from the data of Darbyshire (36). Since the unreliability of the RKR potential (35) appears to be the source of the previous (10) anomalous $\tilde{n}=6$ conclusion, log-log plots similar to Fig. 11 are not presented here. However, it is noted that increasing D by 2.4 cm^{-1} from the previous value (18) to the present one altered the binding energies for the highest levels sufficiently for the last two points on such a log-log plot to display the proper slope of -5.

Steinfeld, Campbell and Weiss (37) calculated RKR turning points for levels $43 \leq v \leq 50$ of I_2 (B $^3\Pi^+_{0u}$), and on analyzing them, concluded that the potential was displaying its theoretical $\tilde{n}=5$ behavior[2] in this region. On the other hand, the results presented in Figs. 5 and 6 suggest that the potential deviates significantly from this asymptotic behavior for $v \lesssim 55$; moreover their (37) apparent C_5 coefficient is more than 100% larger than the theoretical value.[10] Thus, their $\tilde{n}=5$ conclusion appears fortuitous.

Steinfeld et al's (37) turning points for $43 \leq v \leq 51$ were based on their measurement of two vibrational bands whose upper states (they concluded) were $v=43$ and 49. However, their ensuing $v=49$ energy is 11.4 cm^{-1} lower than the value observed by Brown (22), leading to a reassignment of their 49-1 band as 57-2 (see footnote 4, Ref. (11)). This error in energy erroneously compressed the levels $43 < v \leq 49$, and this is the probable source of their apparent R^{-5} behavior.

In Table VI, the "experimental" C_5 values obtained by the present method are compared to the theoretical values.[10] Also given are the approximate binding energies beyond which deviations from simple R^{-5} behavior become apparent, as indicated by Table II and Figs. 2 and 6. These quantities will depend mainly on the relative strengths of the contributing R^{-5}, and R^{-6} and R^{-8} potential terms. It appears that for Br_2 this range is anomalously small in relation to the relative strengths of the C_5 coefficients. However, this may be spurious, due to errors in either the energies or the assignments of the (79,81) levels of Ref. (20).[11]

While the present "experimental" C_5 values are seen to be in reasonable agreement with theory, they are consistently small. Since there may be some residual bias inherent in the present method (2) it is difficult to make an appraisal of the theoretical values, although a potential weakness in them was mentioned in footnote 46 of Ref. (2). However, the qualitative agreement shown in Table VI does strongly confirm that the highest levels considered in the present analysis do depend mainly upon the asymptotically dominant R^{-5} potential tail.

C: General

Recently Stwalley (38) has presented an alternate derivation of Eq.(4),[18] and then applied it to data for the B $^1\Sigma_u^+$ state of H_2 (for which $\tilde{n}=3$) by performing fits to Eq. (7) while varying the value of D to minimize deviations . He also verified the present Eqs. (3-4) for the exact calculated eigenvalues of an LJ (12,3) potential (i.e., a well with an R^{-3} potential tail),[18] obtaining the same good agreement as had previously been found for an R^{-6} -tailed potential (2).

The main restriction on the use of the present method (fits to Eq. (4)) is that the levels considered must lie close enough to the dissociation limit that their Birge-Sponer plot shows positive curvature. It has also been found very advantageous to know the theoretical $\tilde{n}$ for the state under consideration.[2] If in addition the level density is great enough to satisfy the linear approximation of Eq. (5), then application of Eqs. (6-7) may yield good approximations to the best parameter values (see Sec. II). Where appropriate, therefore, plots of the form of Eq. (6) should replace conventional Birge-Sponer extrapolations as a means of determining the dissociation limit D.

It is believed that the present methodology is now sufficiently well documented to become another everyday tool in the spectroscopists' data analysis kit.

Table I: Summary of Results for the Halogens[5]

B $^3\Pi^+_{0u}$ States	D (cm^{-1})^a	n=ñ	C_n [cm^{-1} Å^n]	v_D
$^{35,35}Cl_2$	$20879.7_5(\pm 0.3^b)$	5	$1.2_9(\pm 0.2^b)\times 10^5$	$34.9_0(\pm 0.2^b)$
$^{79,79}Br_2$	$19579.7_1(\pm 0.27)$	5	$1.7_9(\pm 0.2)\times 10^5$	$60.5_1(\pm 0.3)$
$^{81,81}Br_2$	$19581.7_7(\pm 0.35)$	5	$1.7_9(\pm 0.2)\times 10^5$	$61.2_8(\pm 0.3)$
$^{127,127}I_2$	$20044.0\ (\pm 1.2)$	5	$3.1_1(\pm 0.2)\times 10^5$	$87.7\ (\pm 0.4)$
X $^1\Sigma^+_g$ States	$(D=D_o)$			
$^{35,35}Cl_2$	$19997.2_5(\pm 0.3^b)$	6	$0.7_4(\pm 0.3^c)\times 10^5$	$61.0(\pm 1.2^c)$
$^{79,79}Br_2$	$15894.5(\pm 0.4)$	6	—	—
$^{81,81}Br_2$	$15896.6(\pm 0.5)$	6	—	—
$^{127,127}I_2$	$12440.9(\pm 1.2)$	6	—	—

a) See footnotes 3 and 7.

b) See footnote 6.

c) These uncertainties are only estimates.

Table II: Calculated energies (in cm^{-1}) of the highest bound levels of isotopic $Br_2(B\ {}^3\Pi^+_{0u})$. Numbers in parentheses are experimental; for (79,79) and (81,81) these are from Ref. (18), while for (79,81) they are taken from Ref. (20). 11

v	(79,79)		(79,81)		(81,81)	
41	19453.44		19448.89	(19470.3)	19444.00	
42	473.76		469.72	(486.2)	465.37	
43	491.66		488.13	(499.5)	484.31	
44	507.34		504.28	(512.5)	500.97	
45	520.94		518.36	(524.3)	515.53	
46	532.65		530.51	(531.5)	528.15	
47	542.62		540.90	(542.2)	538.98	
48	551.01		549.68	(551.4)	548.18	
49	557.97		557.01		555.90	
50	563.65	(19563.65)	563.04		562.28	(19562.28)
51	568.20	(568.20)	567.90		567.46	(567.45)
52	571.76	(571.77)	571.74		571.60	(571.61)
53	574.47	(574.47)	574.69		574.82	(574.81)
54	576.46		576.89		577.24	
55	577.84		578.46		579.00	
56	578.75		579.51		580.22	
57	579.2_9		580.1_7		581.00	
58	$579._{57}$		$580._{53}$		581.4_5	
59	$579._{69}$		$580._{69}$		$581._{68}$	
60	$579._{71}$		$580._{74}$		$581._{76}$	
61	—		—		$581._{77}$	

Table III: Calculated energies (in cm^{-1}) of the highest bound levels of $^{127,127}\mathrm{I}_2(\mathrm{B}\ ^3\Pi^+_{0u})$. Brown's (22) experimental energies for v $\leq$ 72 are given in parentheses.

v	E(v)	v	E(v)
66	19987.2 (19986.9)	77	20038.6
67	995.5 (995.5)	78	040.1
68	20002.8 (20002.7)	79	041.3
69	009.4 (009.6)	80	042.2
70	015.2 (015.5)	81	042.$_9$
71	020.2 (020.2)	82	043.$_3$
72	024.7 (024.4)	83	043.$_6$
73	028.5	84	043.$_{84}$
74	031.7	85	043.$_{94}$
75	034.4	86	043.$_{99}$
76	036.7	87	044.$_{00}$

Table IV: Calculated energies (in cm^{-1}) of the highest bound levels of ground-state $^{35,35}C\ell_2(X^1\Sigma_g^+)$. The experimental level energies, obtained by applying the rotational reassignment of Ref. (15) to the data of Ref. (14), are given in parentheses.

v	E(v)	v	E(v)
48	19119.	55	19911. (19905.[a])
49	306. (19305.[a])	56	947.
50	465.	57	972.
51	597.	58	986.
52	706. (19711.[a])	59	994.
53	792.	60	996.$_{8}$[b]
54	860.	61	997.$_{25}$[b]

a) Calculated from the data in Table I of Ref. (14) using the rotational reassignment of Ref. (15) and the ground-state rotational constants of Ref. (9).

b) Within the uncertainty in v_D (see Table I), these levels may not exist.

Table V: Binding energies (in cm^{-1}) of highest observed level (v_H) of the B $^3\Pi^+_{0u}$ states of the halogens

Species	v_H	Present	Previous
$^{35,35}Cl_2$	31	$2.8_5(+0.3)$[a]	$3._1(\pm 2.)$[b]
$^{79,79}Br_2$	50	$5.2_4(\pm 0.2_7)$	$2.7(\pm 0.5)$[c]
$^{81,81}Br_2$	50	$6.9_6(\pm 0.3_5)$	$4.1(\pm 0.5)$[c]
$^{127,127}I_2$	72	$19.6(\pm 1.2)$	12.6[d]

a) See footnote 6.

b) From Ref. (9).

c) From Ref. (18).

d) From Ref. (22).

Table VI: Comparison of present "experimental" C_5 values (in cm^{-1} $\mathring{A}^5$) with theoretical estimates\10/ for the B $^3\Pi^+_{0u}$ states of the halogens. $E_b(\tilde{n} = 5)$ is the approximate binding energy beyond which deviations from R^{-5} behavior become apparent.

Species	$C\ell_2$	Br_2	I_2
C_5 "Experimental"	$1.2_9(\pm 0.2)\times 10^5$	$1.7_9(\pm 0.2)\times 10^5$	$3.1_1(\pm 0.2)\times 10^5$
C_5 Theoretical[a]	$1.4_4\times 10^5$	$2.3_9\times 10^5$	$4.5_4\times 10^5$
E_b ($\tilde{n}$=5) [cm^{-1}]	60	50[b]	200

[a] See footnote 10.

[b] As discussed in footnote 11, the isotopic assignments of Brown's (20) levels may be in error, in which case this 50 cm^{-1} is a lower bound to $E_b(\tilde{n}=5)$.

Footnotes

1. Eq. (4) is valid only for cases in which $n \neq 2$. However, analogous expressions for $n=2$ and for the case of an attractive exponential long-range potential are given in Ref. (2).

2. A summary of theoretical knowledge of the asymptotically dominating power $\tilde{n}$ is given in Appendix B of Ref. (2). For the B $^3\Pi^+_{0u}$ states of the halogens $\tilde{n}=5$, while for their ground X $^1\Sigma_g^+$ states, $\tilde{n}=6$ (6,7,8).

3. Unless otherwise stated, throughout this paper all energies are expressed relative to the $v=0$, $J=0$ level of the ground electronic state of the designated isotopic molecular species.

4. The present discussion of chlorine considers only the most common isotopic species, $^{35,35}Cl_2$.

5. Unless otherwise stated, all uncertainties given in this paper correspond to 95% statistical confidence intervals.

6. The final uncertainties in the best parameter values for Cl_2 (B $^3\Pi^+_{0u}$) differ from both the previously reported values (1,2) and the true 95% statistical confidence intervals shown in Fig. 1. The values given are best estimates based on the 95% confidence intervals for the last few points to the right in Fig. 1.

7. The uncertainties in these D values differ from those reported previously (1,2,11) because of the incorrect 95% confidence intervals in the earlier work.

8. This is much less stringent than requiring precise potential invariance everywhere, including R values near the minima. Small differences between potential curves for different isotopic species in a given state arise from the coupling of nuclear and electronic motion. In their *a priori* calculations for the ground state of H_2, Kolos and Wolniewicz (16) showed that the effect of such coupling disappeared at long range. More generally, the effect of this coupling on an eigenvalue depends on the expectation value of the nuclear kinetic energy, and this goes to zero for levels approaching the dissociation limit (e.g., for ground state H_2, see Table III of Ref. (17)).

9. These shifts were estimated in two ways: (a) by comparing vibrational zero point energies, and (b) by separately smoothing the level energies for the different isotopic molecules as functions of a common abscissa χ (related to the vibrational quantum number by: $\chi = v(i)\,[\mu(1)/\mu(i)]^{\frac{1}{2}}$) and comparing the calculated ordinates at any chosen χ value.

10. Values of long-range C_5 constants may be expressed as the product of a factor peculiar to the electronic state in question, and the expectation values of the square of the radii of the valence electrons $\langle r^2 \rangle$ on the interacting atoms (6). Knipp (6) and Chang (7) have presented tables of these numerical factors for a wide range of situations, and Fischer (19) has recently presented accurate Hartree-Fock values of $\langle r^2 \rangle$ for shells of most atoms.

11. Brown (20) stated that: "In general the measurements are not accurate to better than 2 cm^{-1}, and in cases where the isotope effect has not been identified, the error is considerably greater." Furthermore, consideration of Table II suggests that some of his band heads might more properly be reassigned to the pure isotopes. If this is done, for 6 of the 8 experimental (79,81) energies given in Table II the agreement is better than 2 cm^{-1}, while for the other two ($v=44$ and 45) the disagreement is at worst 3.5 cm^{-1}. In any case, the calculated (Table II) energies for the deeper levels (e.g., $v \lesssim 43$) are likely to be increasingly in error.
12. The present discussion of iodine considers only the most common isotopic species $^{127,127}I_2$.
13. The original vibrational numbering of these levels has since been revised (23,24); thus the numbering used by Brown (22) has been decreased by one unit.
14. Using their rotational reassignment, Clyne and Coxon (15) obtained a D_o value 43 cm^{-1} larger than the present estimate; however, this change does not affect the qualitative arguments presented here.
15. The scatter in the doublet splittings (14) which give the B_v values for the upper states is large enough to yield possible errors of a few cm^{-1} in the level energies.
16. For an excellent review of these methods, see chapter V of the book by Gaydon (33).

17. The $v=32$ turning point reported by Todd et al (35) is ignored here as being spurious, since there is no reported observation of this level. This point would lie well above all the lines in Fig. 11, since their extrapolated [E(32)-E(31)] is some 30% smaller than that predicted (2) on substituting the constants of Table I into Eq. (4).

18. In Stwalley's more approximate derivation, a numerical factor of $\pi/2$ occurs in place of the ratio of gamma functions in Eq. (3) (38). For a given fitted value of H_n, use of his numerical factor would give values of C_n for $n=3$ and 6 which are too large by factors of 1.41 and 4.68 respectively.

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Figure Legends

Figure 1 Results of fitting experimental vibrational energies of $^{35,35}\mathrm{C}\ell_2$ (B $^3\Pi^+_{0u}$) (9) to Eq. (4). The points correspond to fits of levels v_L up to $v_H = 31$. The broken vertical line is the best estimate obtained for D. Points joined by solid curves correspond to four-parameter fits with n varied freely, while the others correspond to three-parameter fits with n held fixed at $\tilde{n} = 5$. The error bars represent proper 95% confidence intervals.

Figure 2 Data for $^{35,35}\mathrm{C}\ell_2$ (B $^3\Pi^+_{0u}$) (9) plotted according to Eqs. (5-6) with $n=\tilde{n}=5$.[2] Energies are in cm^{-1}; the mark at D denotes the fitted value from Table I.

Figure 3 Data for $^{35,35}\mathrm{C}\ell_2$ (B $^3\Pi^+_{0u}$) (9) plotted according to Eq. (7) with $n=\tilde{n}=5$.[2] Energies are in cm^{-1}; the mark at v_D denotes the fitted value from Table I.

Figure 4 Data for the (79,79) and (81,81) isotopes of Br_2 (B $^3\Pi^+_{0u}$) (18) plotted according to Eq. (7) with $n=\tilde{n}=5$.[2] As in Fig. 3. The slopes of the lines differ by the amount predicted by the reduced mass factor in Eq. (3).

Figure 5 Results of fitting experimental vibrational energies of $^{127,127}I_2$ $(B\ ^3\Pi^+_{0u})$ (22) to Eq. (4). As in Fig. 1.

Figure 6 Data for $^{127,127}I_2$ $(B\ ^3\Pi^+_{0u})$ (22) plotted according to Eqs. (5-6) with $n=\tilde{n}=5$.[2] As in Fig. 2.

Figure 7 Data for $^{127,127}I_2$ $(B\ ^3\Pi^+_{0u})$ (22) plotted according to Eq. (7) with $n=\tilde{n}=5$.[2] As in Fig. 3.

Figure 8 $[D-E(v)]^{(\frac{n-2}{2n})}$ vs v for observed levels of $^{35,35}C\ell_2$ $(B\ ^3\Pi^+_{0u})$ (9) with D from Table I, for both $n=\infty$ (●, left ordinate scale) and $n=\tilde{n}=5$ (▲, right ordinates). All energies are in cm^{-1}. The broken lines are tangents to the two curves in their linear regions.

Figure 9 $[D-E(v)]^{(\frac{n-2}{2n})}$ vs v for observed levels of $^{35,35}C\ell_2$ $(X\ ^1\Sigma_g^+)$ (14,15) with D from Table I, for both $n=\infty$ (⊙, left ordinate scale), and $n=\tilde{n}=6$ (△, right ordinate scale). All energies are in cm^{-1}. The possible vibrational assignments (points joined by solid lines) correspond to integer values of v on the tie lines for the different levels near their intersections with the linear extrapolation from the two preceding levels (broken lines).

Figure 10 $[D-E(v)]^{\frac{n-2}{2n}}$ vs v for observed (20), solid points) and interpolated (18, open points) levels of $^{79,81}Br_2$ (B $^3\Pi^+_{0u}$) with D from Sec. IIB, for both $n=\infty$(circles, left ordinate scale), and $n=\tilde{n}=5$ (triangles, right ordinates scale). All energies are in cm^{-1}; "old" and "new" refer to the vibrational assignments of the four highest levels.

Figure 11 Log-log plot of binding energies (in cm^{-1}) vs calculated (35) RKR turning points (in Å) for $^{35,35}C\ell_2$ (X $^1\Sigma^+_g$) using both the present (X) and the previous (9) (●) estimates of D.[17] The straight lines have slope of $-n$; the intercept of A corresponds to the present (Table I) C_5, while line B is the best $n=5$ fit to the points for the uppermost levels.

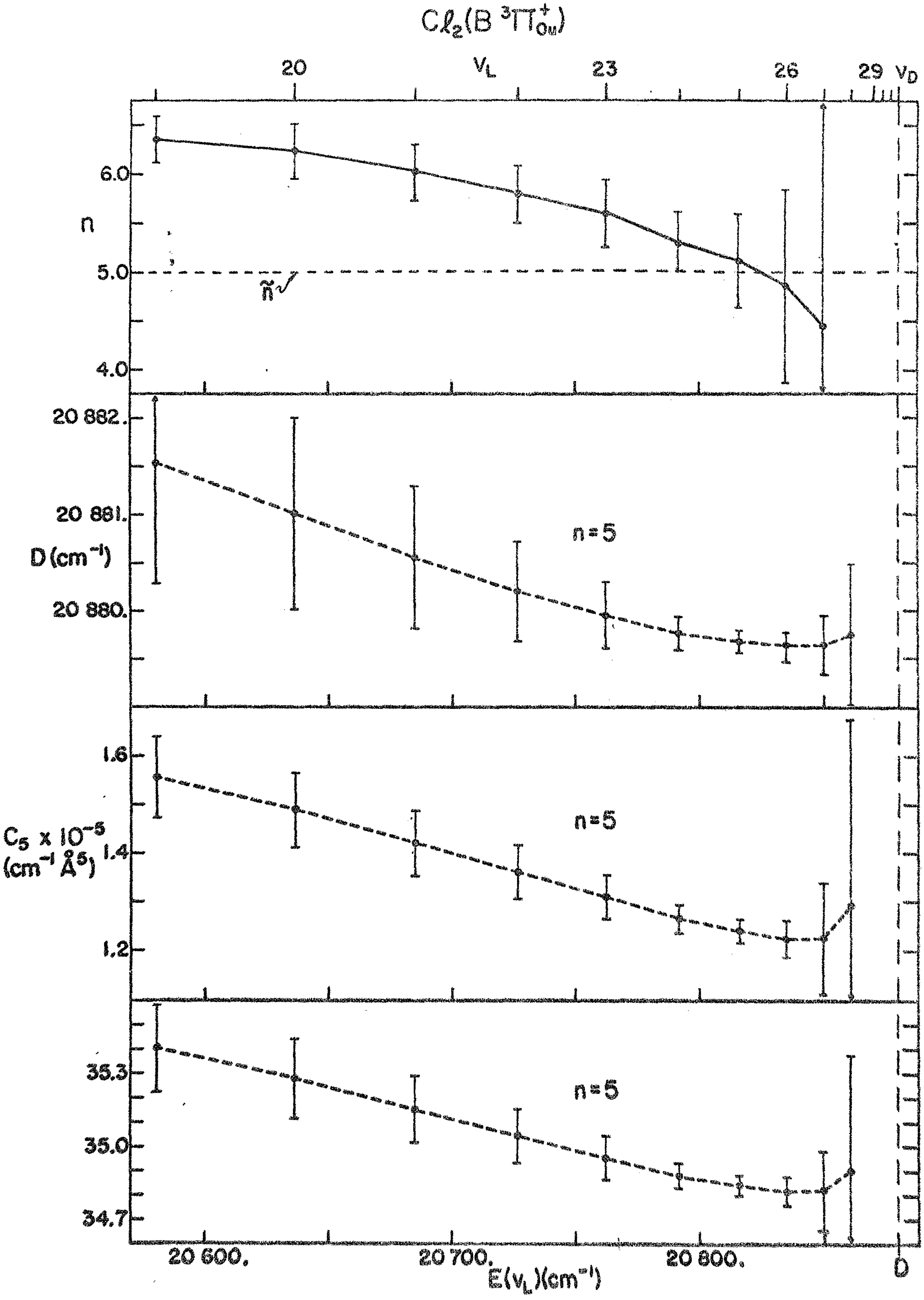
$Cl_2(B\ ^3\Pi^+_{0u})$
20
v_L
23
26
29
v_D
n
6.0
5.0
4.0
$\tilde{n}$
20 882.
20 881.
D (cm⁻¹)
20 880.
n=5
1.6
$C_5 \times 10^{-5}$ (cm⁻¹ Å⁵)
1.4
1.2
n=5
35.3
35.0
34.7
n=5
20 600.
20 700.
20 800.
D
E(v_L)(cm⁻¹)

Figure 1.

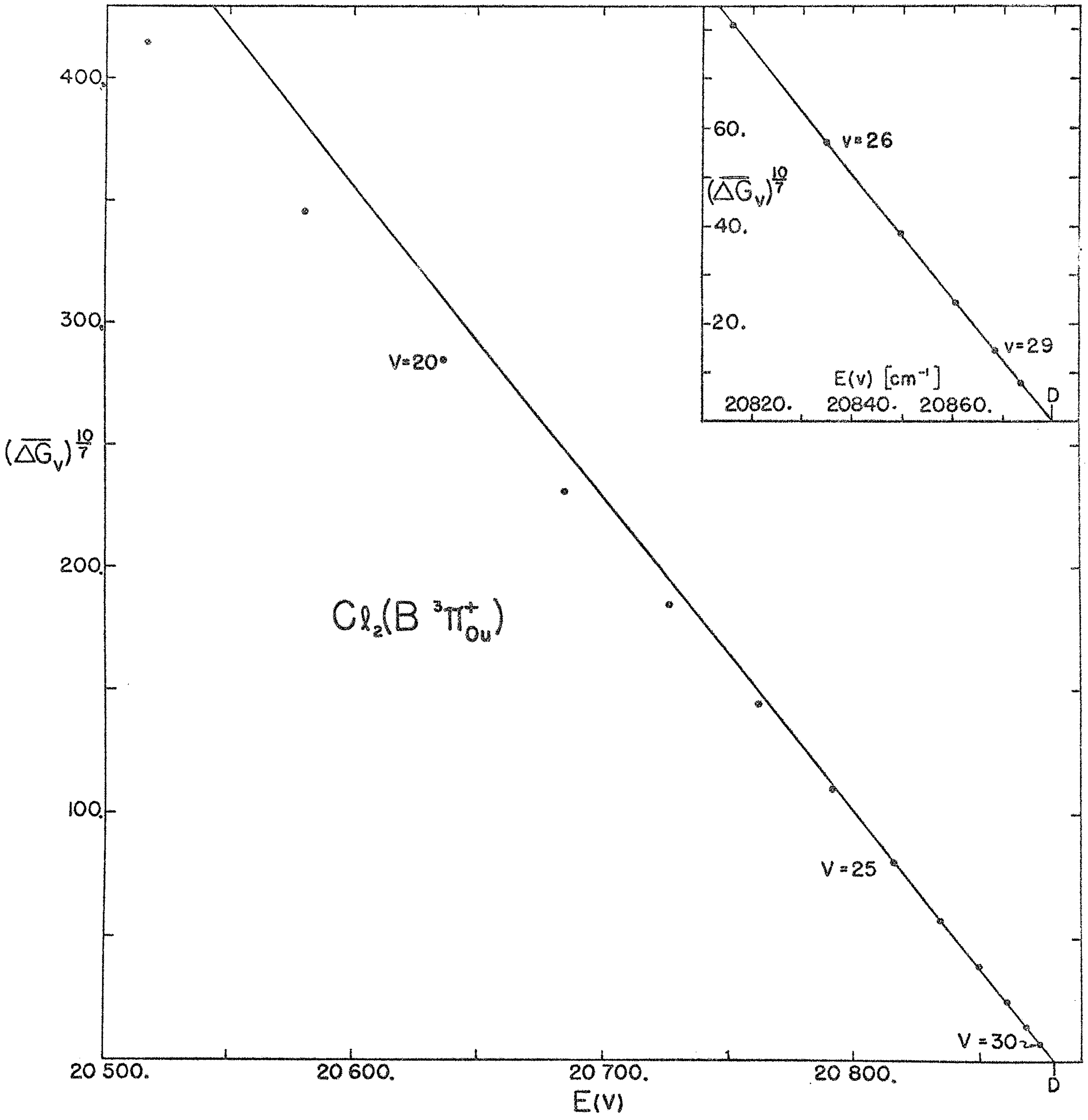
400.
300.
200.
100.
$(\overline{\Delta G}_v)^{\frac{10}{7}}$
V=20
V=25
V=30
D
20 500.
20 600.
20 700.
20 800.
E(V)
$Cl_2(B\ ^3\Pi^+_{0u})$
60.
40.
20.
v=26
v=29
E(v) [cm⁻¹]
20820.
20840.
20860.

Figure 2.

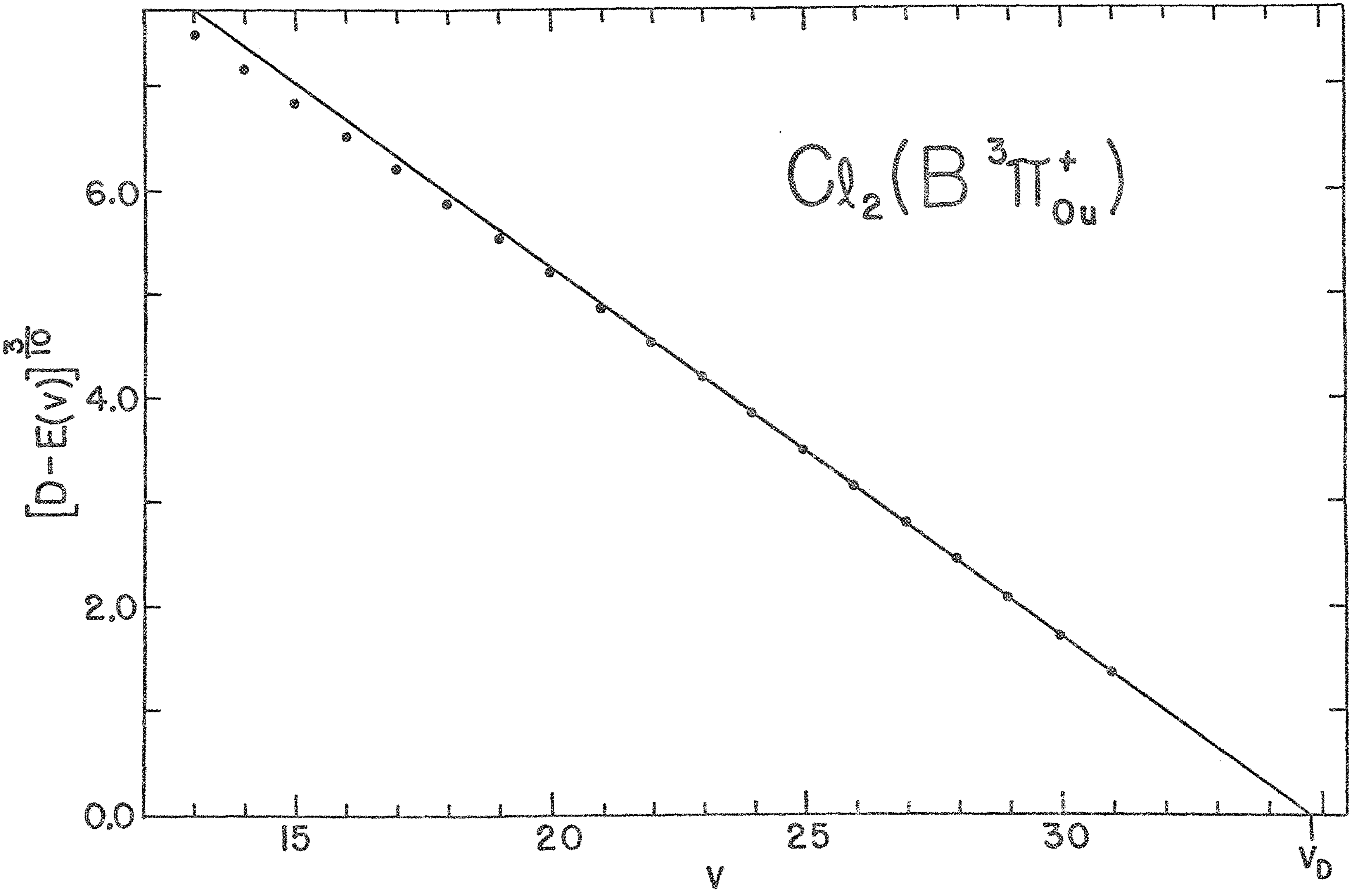

Figure 3.

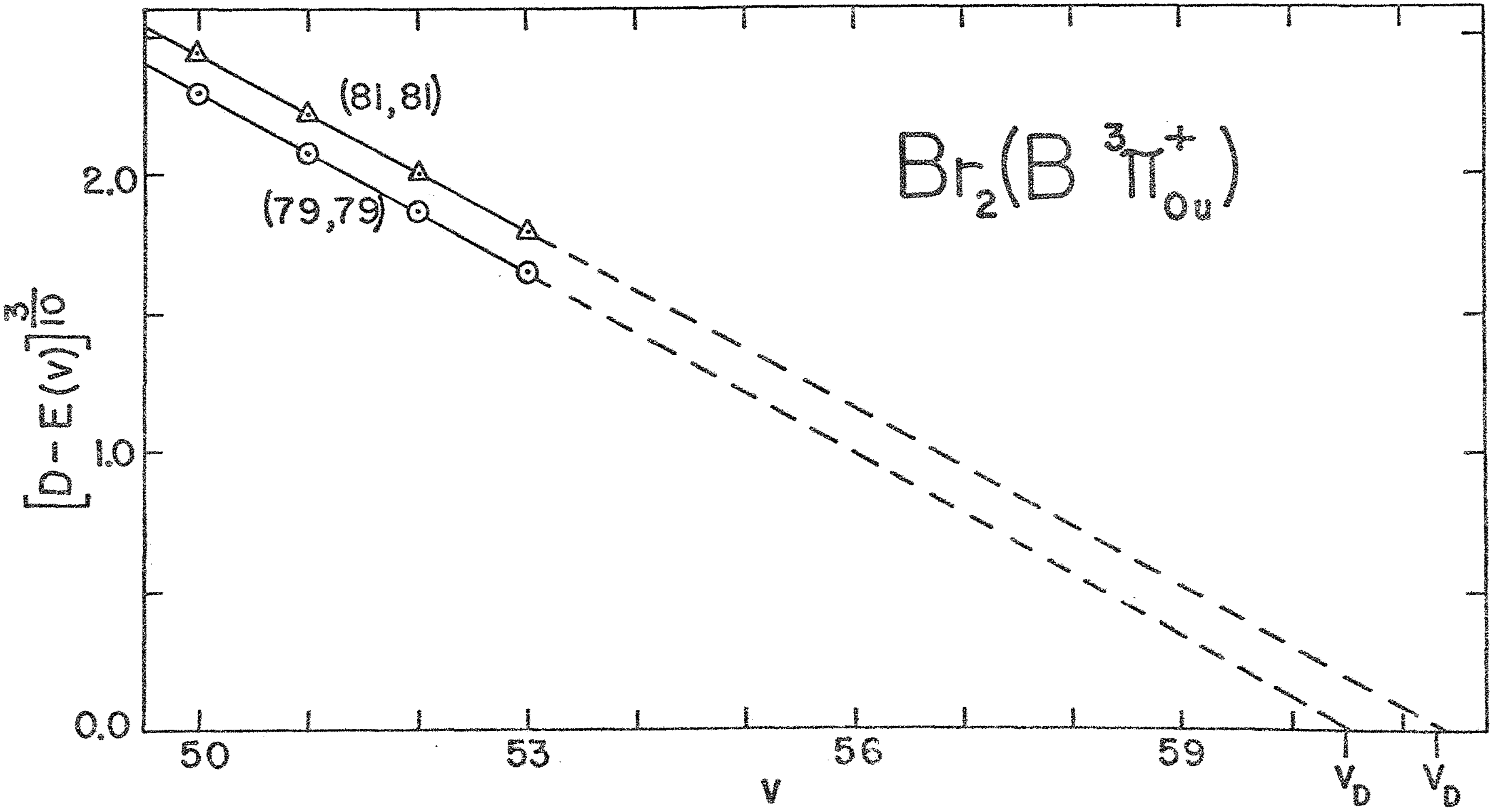

Figure 4.

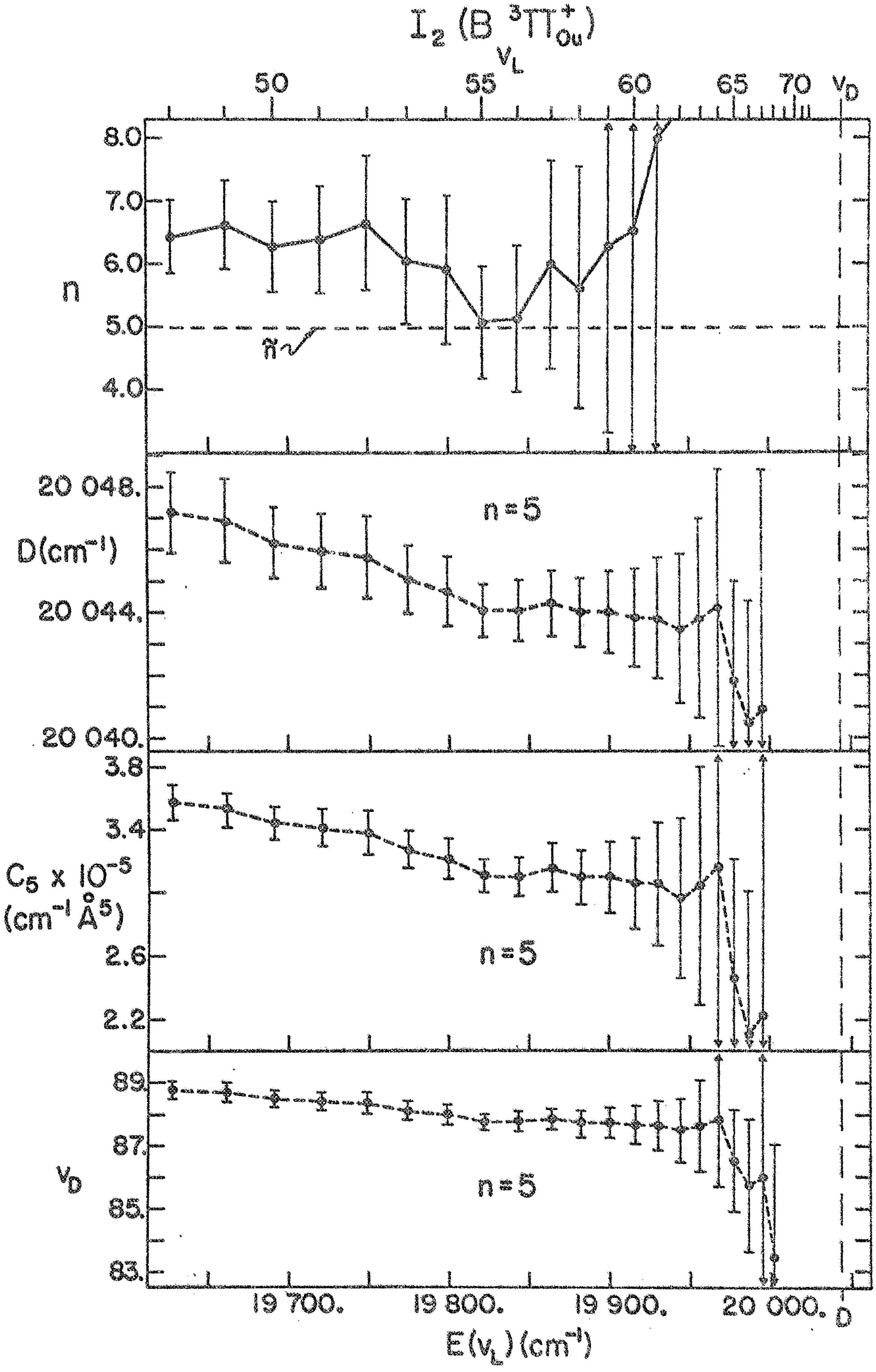
$I_2 (B\ ^3\Pi^+_{0u})$
v_L
50
55
60
65
70
v_D
8.0
7.0
6.0
5.0
4.0
n
$\bar{n}$
20 048.
20 044.
20 040.
D(cm⁻¹)
n=5
3.8
3.4
2.6
2.2
C₅ x 10⁻⁵ (cm⁻¹ Å⁵)
n=5
89.
87.
85.
83.
v_D
n=5
19 700.
19 800.
19 900.
20 000.
D
E(v_L)(cm⁻¹)

Figure 5.

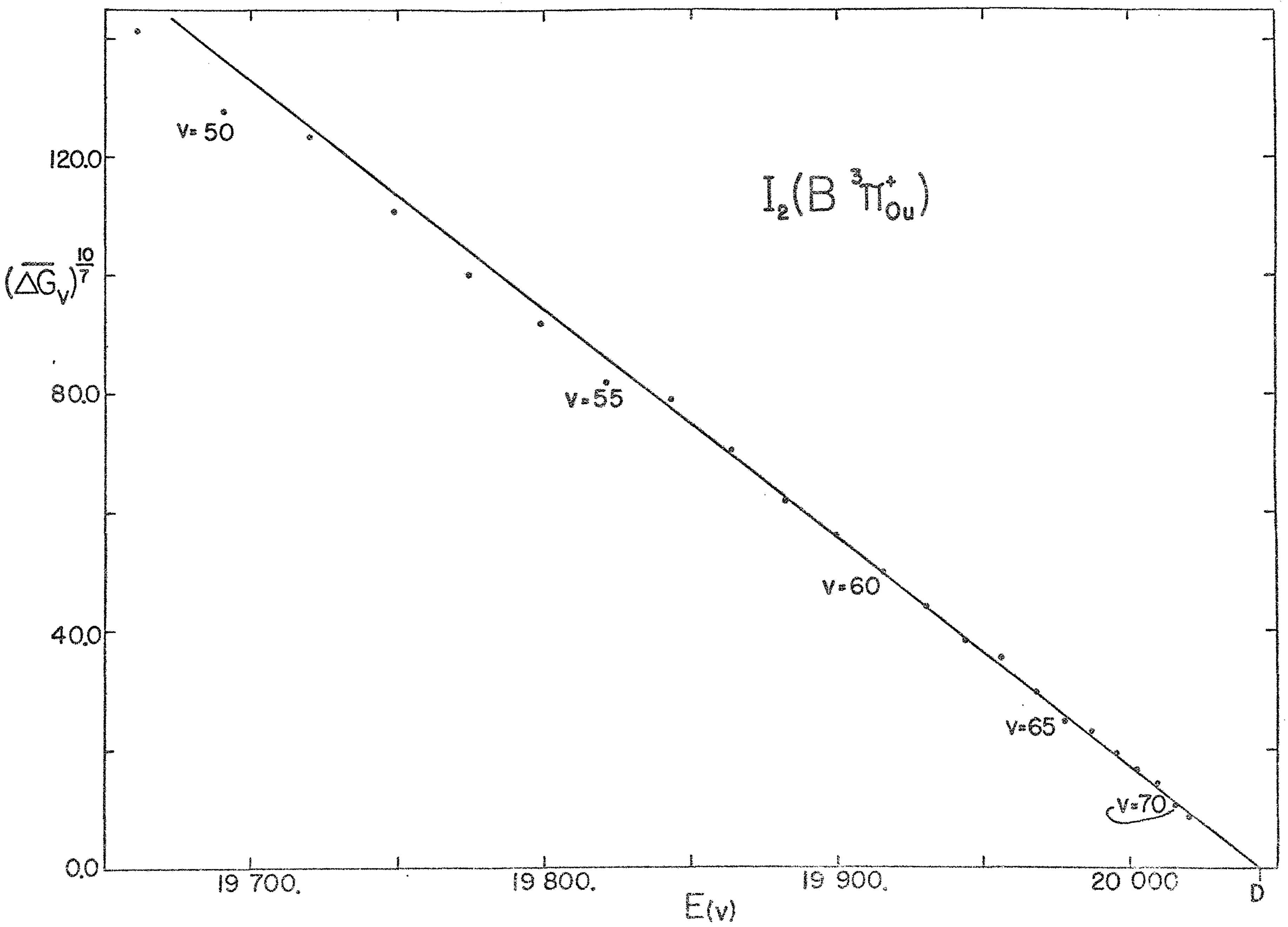
$I_2(B\,{}^3\Pi^+_{0u})$
$(\overline{\Delta G_v})^{\frac{10}{7}}$
120.0
80.0
40.0
0.0
v= 50
v= 55
v= 60
v= 65
v= 70
19 700.
19 800.
19 900.
20 000
D
E(v)

Figure 6.

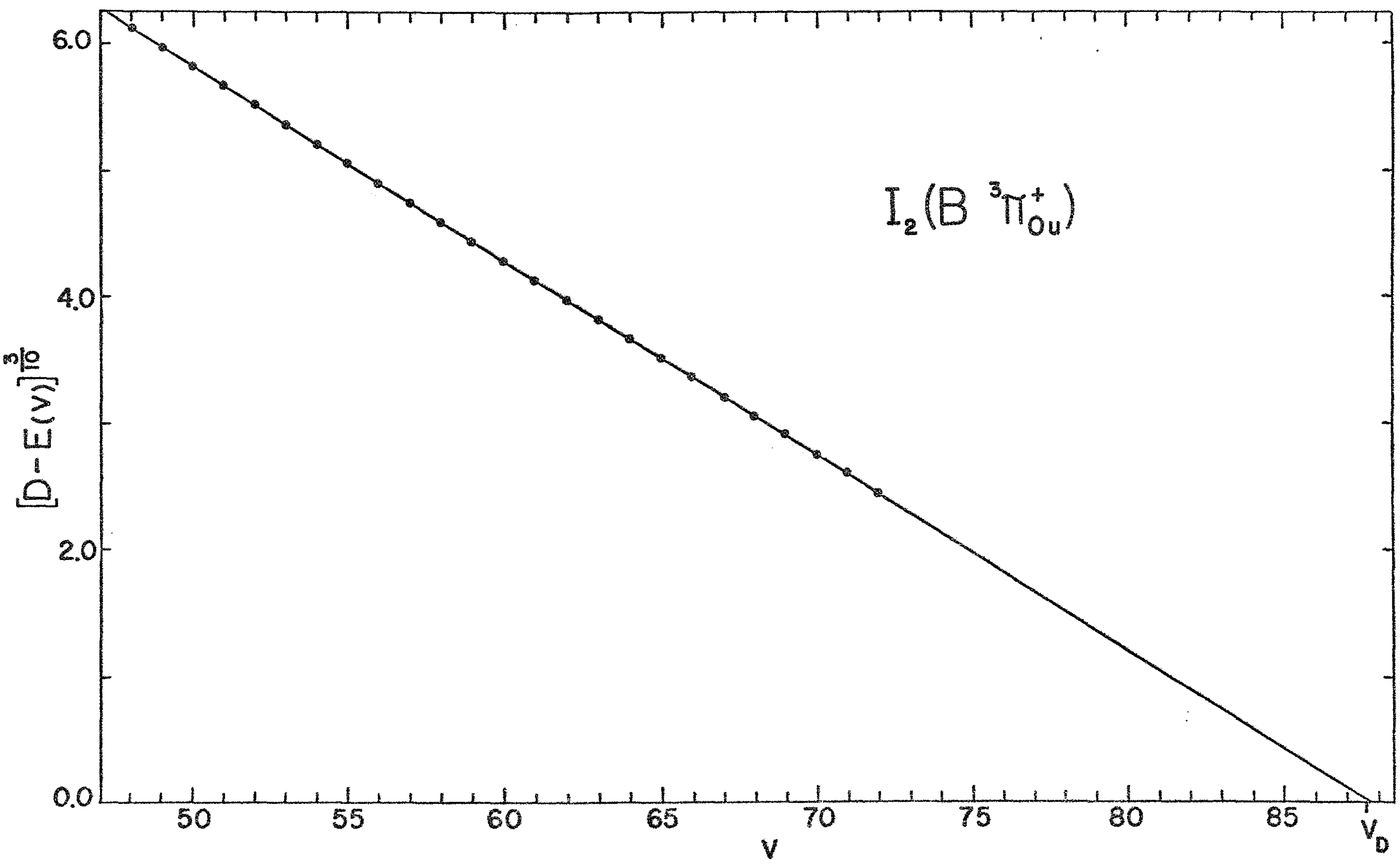

Figure 7.

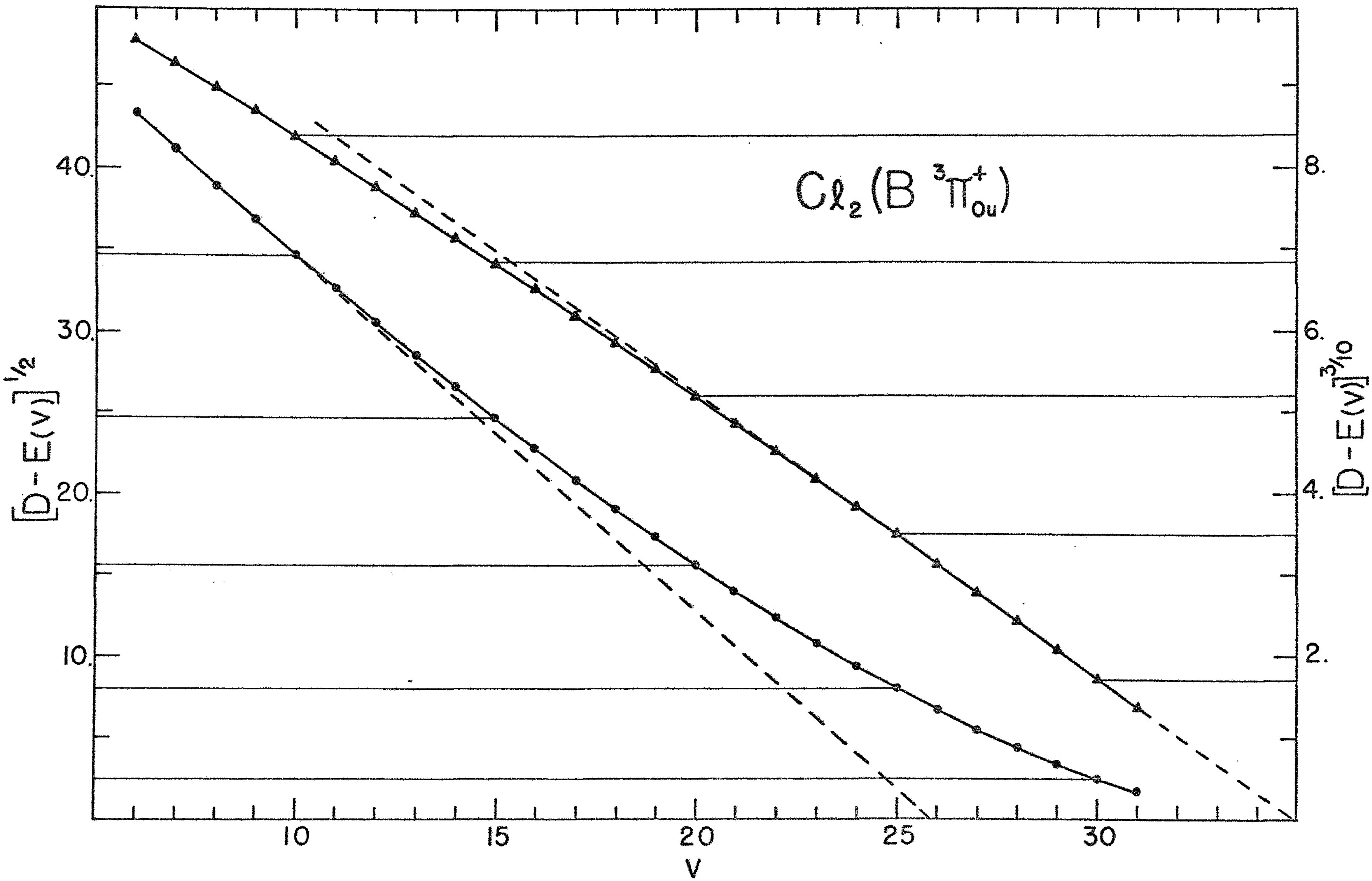

Figure 8.

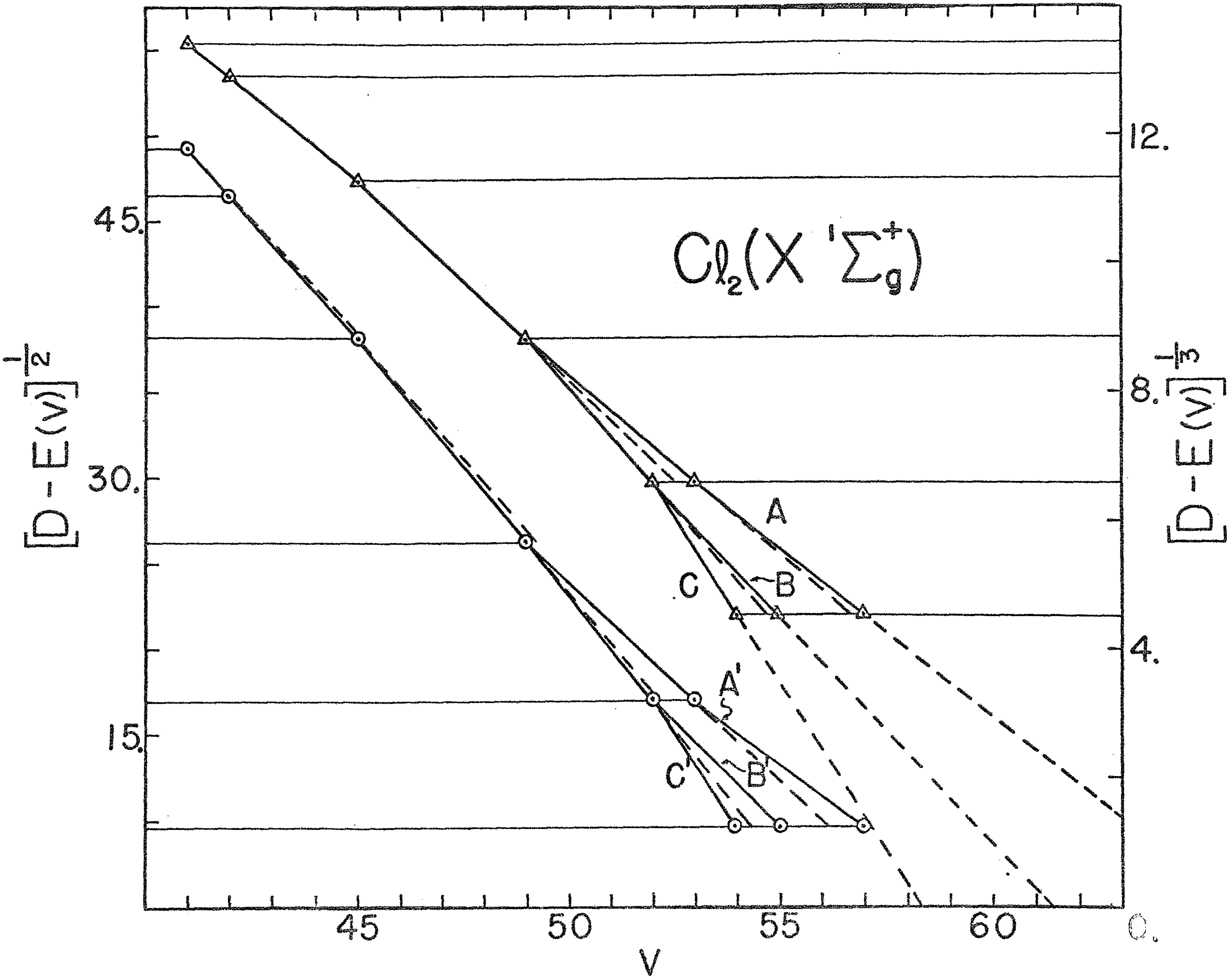
$Cl_2(X\,^1\Sigma_g^+)$
$[D-E(v)]^{-\frac{1}{2}}$
45.
30.
15.
$[D-E(v)]^{-\frac{1}{3}}$
12.
8.
4.
0.
45
50
55
60
V
A
B
C
A'
B'
C'

Figure 9.

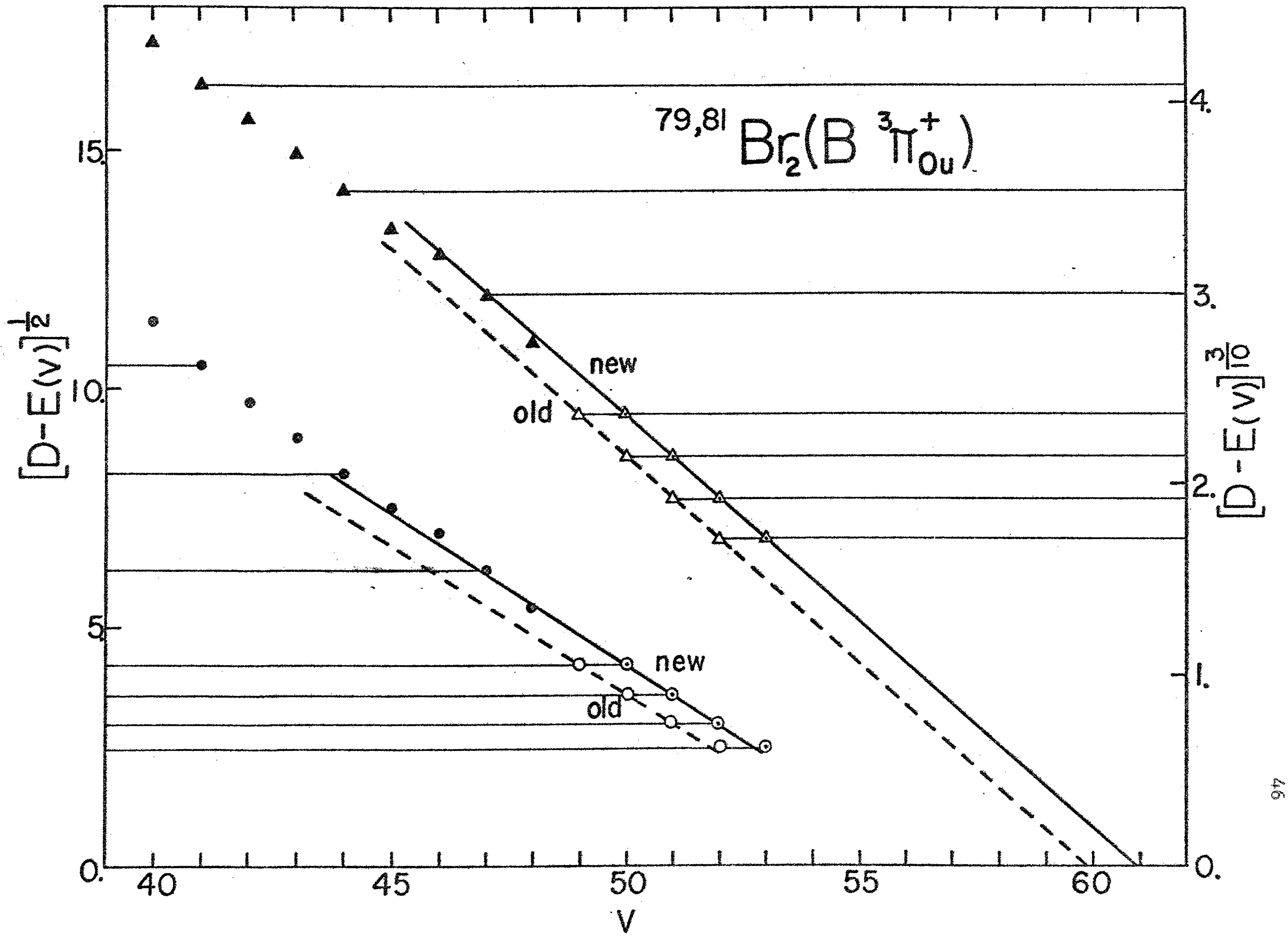
$^{79,81}Br_2(B\ ^3\Pi^+_{0u})$
$[D-E(v)]^{\frac{1}{2}}$
$[D-E(v)]^{\frac{3}{10}}$
V
new
old
new
old
0.
5.
10.
15.
40
45
50
55
60
0.
1.
2.
3.
4.

Figure 10.

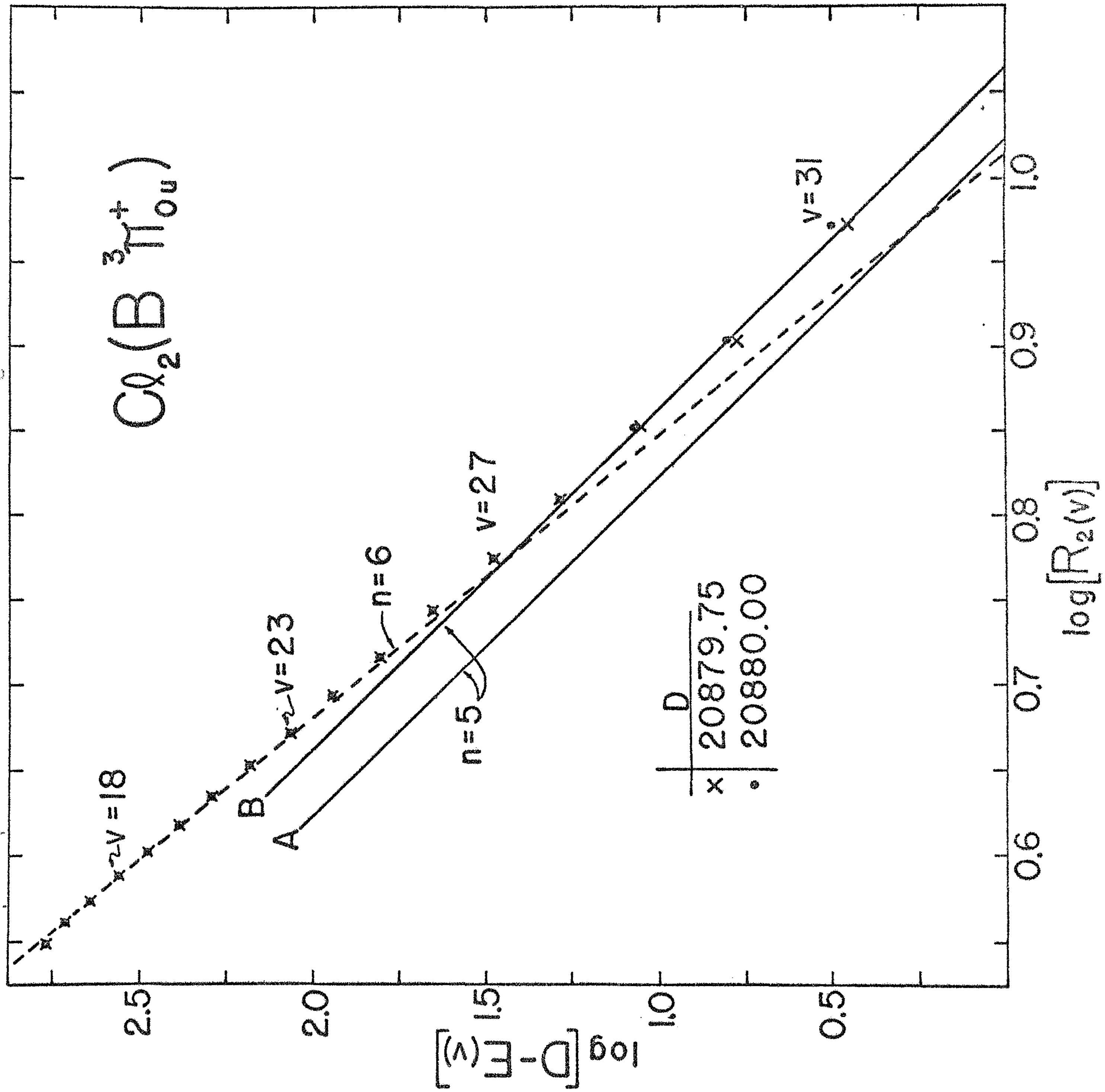
Cl₂(B ³Π⁺₀ᵤ)
v=18
v=23
v=27
v=31
n=6
n=5
A
B
D
× 20879.75
• 20880.00
2.5
2.0
1.5
1.0
0.5
log[D-E(v)]
0.6
0.7
0.8
0.9
1.0
log[R₂(v)]

Figure 11.

Appendix A: Smoothing and Fitting Program to Obtain Trial Parameter Values

A Fortran V listing of the smoothing and fitting program used to obtain good trial parameter values for use in the general non-linear fits to Eq. (4) (see Appendix B) is presented below. In addition to the approaches discussed above and in Ref. (2), for cases in which at least one of the parameters is known the alternate fitting procedures described below may be used.

Case 1: If $n=\tilde{n}$ is known,^{2} Eq. (2) may be written as

$$[dE(v)/dv]^{\left(\frac{2n}{n+2}\right)} = [D-E(v)]\,K_n^{\left(\frac{2n}{n+2}\right)} , \qquad (A1)$$

so that a linear fit to $[dE(v)/dv]^{\left(\frac{2n}{n+2}\right)}$ vs. $E(v)$ yields D as the intercept, and C_n (from K_n, see Eq. (3)) from the slope. Subsequently, v_D may be obtained from Eq. (7). In effect, Eq. (A1) is equivalent to Eq. (6) except that the derivative is obtained by polynomial smoothing rather than by the approximation of Eq. (5).

Case 2: If D is known, Eq. (2) yields

$$\log\,[dE(v)/dv] = \log\,(K_n) + \left(\frac{n+2}{2n}\right)\log\,[D-E(v)] , \qquad (A2)$$

which suggests a linear fit to log [dE(v)/dv] vs. log [D-E(v)] to obtain n and C_n. Analogous to Eq. (6), the approximation of Eq. (5) yields

$$\log(\overline{\Delta G_v}) = \log(K_n) + \left(\frac{n+2}{2n}\right) \log[D-E(v)] \ , \qquad (A3)$$

which may be used in the same manner as Eq. (A2). In either case, a subsequent fit to Eq. (7) yields v_D.

Case 3: If both $n=\tilde{n}$ and D are known, Eq. (4) may be written as

$$[D-E(v)]^{\left(\frac{n-2}{2n}\right)} = (v_D-v)\ H_n \ , \qquad (A4)$$

and the linear fit suggested by this expression yields v_D and H_n (and hence C_n).

The fitting procedure used in a given case is determined by the value of the parameter IDR2 read in as input. The three basic approaches which have been discussed: a) use of Eqs. (15-16) in Ref. (2) (IDR2>0), b) use of Eqs. (A1-A2) and Eq. (7) (IDR2=0), and c) use of Eqs. (5-7) and Eqs. (A3-A4) (IDR2<0), have all been tested. Except in cases where there is much scatter in the data, procedure a) appears to give significantly better fits than the others; however the results of the other approaches are also satisfactory.

```
C***  PROGRAM FOR APPROXIMATE FITTING OF  VIBRATIONAL ENERGIES TO
C   LE ROY - BERNSTEIN WKB-BASED EXPRESSION FOR HIGHLY EXCITED
C   VIBRATIONAL LEVELS, YIELDING GOOD TRIAL PARAMETERS FOR GENERAL
C   NON-LINEAR FIT TO THE GENERAL EXPRESSION.   PARAMETERS ARE
C   THE  DISSOCIATION LIMIT  D, THE POWER  N  AND COEFFICIENT  CN  OF
C   THE EFFECTIVE LOCAL INVERSE-POWER POTENTIAL, AND THE INTEGRATION
C   CONSTANT  VD , WHICH FOR (N.GT.2) CORRESPONDS TO THE VIBRATIONAL
C   INDEX AT THE DISSOCIATION LIMIT. *** PROGRAM CAN CONCURRENTLY FIT
C   DATA FOR DIFFERENT ISOTOPES OF A GIVEN SPECIES, USING A COMMON  N
C   AND  CN, WHILE RELATING THE  VD  VALUES THROUGH THE (KNOWN) RATIO
C   OF THE REDUCED MASSES, AS LONG AS THE RELATIVE ISOTOPIC ZERO-POINT
C   ENERGY SHIFTS ARE EITHER KNOWN, OR MAY BE ESTIMATED FROM THE DATA.
C*** PROGRAM WRITTEN AND TESTED BY R.J. LE ROY.
      DIMENSION  E(50),VF(50),R2(50),TITL(16),BZ(4),SBZ(4),FMU(4),SH(4),
     1  DSH(4),VDIS(4),AA(11)
      COMMON/BLK1/T(50),X(50),Y(50),DG(50),D2G(50),RAT(50),DY1(50),
     1  DY2(50),X2(50),W(50)
      DATA/T/12.706,4.303,3.182,2.776,2.571,2.447,2.365,2.306,2.262,
     1  2.228,2.201,2.179,2.160,2.145,2.131,2.120,2.110,2.101,2.093,
     2  2.086,2.080,2.074,2.069,2.064,2.060,2.056,2.052,2.048,2.045,
     3  2.042,20*2.000/
      DO 1 I=1,50
    1 W(I)=1.0
      PI=3.1415926
      SQPI=SQRT(PI)
C*** TITL  IS THE NAME OF THE SYSTEM CONSIDERED.
C*** NISOT  IS THE NO. OF DIFFERENT ISOTOPES CONSIDERED AT ONCE.
C*** NCAS  IS THE NO. OF DIFFERENT FITS TO BE MADE TO THE DATA FOR
C   THIS SYSTEM.
C*** IF(ISH.GT.0) WHERE (NISOT.GT.1), SHIFT ENERGIES FOR DIFFERENT
C   ISOTOPES BY KNOWN INITIAL-STATE ISOTOPE SHIFTS.
    2 READ(5,502)  (TITL(I),I=1,16),NISOT,NCAS,ISH
      IF(NCAS.LE.0) GO TO 999
      NUB=10
      ICAS=0
      IF(NISOT.LE.1) ISH=0
C** FIT POLYNOMIALS OF INCREASING ORDER TO GIVEN ENERGIES UNTIL STDERR
C   CONVERGES, OR BECOMES LESS THAN THE PRECISION OF THE DATA,  ERY.
C*** BZ  IS A NUMERICAL FACTOR FOR EACH ISOTOPE INCLUDING REDUCED MASS
C   ETC  BZ=8*PI**2*MU(AMU)*1.(1/CM)*(1.(ANGST))**2/H**2
      READ(5,503)  ERY,(BZ(J),J=1,NISOT)
      IWRST=1
      WRITE(6,601) (TITL(I),I=1,16),ERY,NISOT,(BZ(I),I=1,NISOT)
      NLV=0
      IS=0
      SH(1)=0.0
      IF(ISH.LE.0) GO TO 4
      READ(5,503)  (SH(J),J=2,NISOT)
      WRITE(6,618) (J,SH(J),J=2,NISOT)
    4 IS=IS+1
      SBZ(IS)=SQRT(BZ(IS))
      FMU(IS)=SBZ(1)/SBZ(IS)
C*** NIS  IS THE NO. OF LEVELS READ IN FOR ISOTOPE (IS)
C*** IF(IVH.LT.0) READ IN ENERGIES AND VIB NUMBERING TOGETHER.
C   IF(IVH.GE.0) NUMBER VIB LEVELS DOWN FROM V=IVH FOR HIGHEST.
      READ(5,501)  NIS,IVH
```

```
      NLB=NLV
      NL1=NLV+1
      NLV=NLV+NIS
C*** READ IN LEVEL ENERGIES IN UNITS OF (1/CM), HIGHEST LEVELS FIRST.
      IF(IVH.LT.0) GO TO 8
      READ(5,503) (E(I),I=NL1,NLV)
      DO 6 I=1,NIS
    6 VF(NLB+I)=IVH+1-I
      GO TO 10
    8 READ(5,504) (VF(I),E(I),I=NL1,NLV)
   10 IF(IS.EQ.1) GO TO 30
      DO 12 I=NL1,NLV
   12 VF(I)=VF(I)*FMU(IS)
      IF(ISH.GT.0) GO TO 16
C*** ESTIMATE ISOTOPE SHIFTS FOR (IS.GT.1) BY COMPARISONS WITH DATA FOR
C    ISOTOPES CONSIDERED ALREADY.
      SM=0.0
      SM2=0.0
      DO 14 I=NL1,NLV
      XX=VF(I)-VF(1)
      N1=NU+1
      DF=AA(N1)
      DO 13 J=1,NU
   13 DF=XX*DF+AA(N1-J)
      DF=E(I)-DF-E(1)
      SM=SM+DF
   14 SM2=SM2+DF**2
      SH(IS)=SM/NIS
      DSH(IS)=T(NIS-1)*SQRT((SM2-NIS*SH(IS)**2)/(NIS-1))/
     1  SQRT(FLOAT(NIS))
      WRITE(6,617) IS,SH(IS),DSH(IS)
C*** CORRECT DATA BY INCLUDING ISOTOPE SHIFT
   16 DO 18 I=NL1,NLV
   18 E(I)=E(I)-SH(IS)
C*** COMBINE AND ORDER DATA FOR DIFFERENT ISOTOPIC SPECIES, HIGHEST 1-ST.
      JI=1
      DO 28 J=NL1,NLV
      JF=J-1
      DO 20 I=JI,JF
      K=I
      IF(VF(J).GT.VF(I)) GO TO 22
   20 CONTINUE
      GO TO 30
   22 VFF=VF(J)
      EE=E(J)
      JI=K+1
      DO 24 I=JI,J
      L=J+JI-I
      VF(L)=VF(L-1)
   24 E(L)=E(L-1)
      VF(K)=VFF
      E(K)=EE
   28 CONTINUE
   30 IF(IS.GE.NISOT) GO TO 38
      IF(ISH.GT.0) GO TO 4
```

```
C*** LEAST SQUARES FITTING WHEN REQUIRED TO GET SHIFT FOR NEXT ISOTOPE.
      NU=3
      NUB=10
      DO 34 I=1,NLV
      X(I)=VF(I)
   34 Y(I)=E(I)
      ID2=-1
      NU=1
      CALL PLYFIT(NLV,NU,NUB,AA,ERY,ID2)
      WRITE(6,616) IS,NU
      GO TO 4
   38 ICAS=ICAS+1
C*** FIT THE FIRST  NFT  LEVELS, STARTING BELOW THE HIGHEST  ND1 OF THEM
C*** IF(NDT.LT.0) DROP DEEPER LEVELS FROM FIT ONE AT A TIME.
C*** IF(NDT.GT.0) REPEATEDLY FIT SAME NO. OF LEVELS WHILE SUCCESSIVELY
C   OMITTING HIGHER ONES,  NDT AT A TIME. USE THIS OPTION TO YIELD THE
C   EFFECTIVE LOCAL POTENTIALS.
C*** NHD  IS THE NO. OF CONSTANTS TO BE HELD CONSTANT.
C*** IF(NHD.EQ.1) FIX  N=HD1,  IF(NHD.EQ.-1) FIX  DISOC=HD1.
C*** IF(NHD.EQ.2) FIX BOTH  N=HD1  AND  CN=HD2.  IF(NHD.EQ.-2) FIX
C   BOTH  N=HD1  AND  DISOC=HD2
C*** IDR2  DEFINES THE VARIOUS FITTING MODES. ** IF(IDR2.GT.0) FIT
C   USING EQS.(15-16) IN J.CHEM.PHYS.,VOL.52,3869(1970).
C** IF(IDR2.EQ.0) FIT USING EQS.(A1-A2) OF REPORT  WIS-TCI-369(1970).
C ** IF(IDR2.LT.0) USE EQS.(5-7, AND A3-A4) OF  WIS-TCI-369(1970). IN
C   THIS CASE, IF((NISOT.EQ.1).AND.(NHD.NE.-2)) THERE CAN BE NO GAPS
C   OF UNOBSERVED LEVELS IN THE ENERGIES USED.
      READ(5,501) NFT,ND1,NDT,NHD,IDR2
      IF(NHD.EQ.0) IDR2=1
      IF((IDR2.EQ.0).AND.(NHD.EQ.-2)) IDR2=-1
      IF((IDR2.LT.0).AND.((ABS(VF(1)-VF(2)-1.).GT.0.01).OR.(NISOT.GT.1)
     1  )) IDR2=0
      NHDA=NHD
      IF(NHD.LT.0) NHDA=-NHD
      NUB=10
      IST=ND1
      IF(NHD.NE.0) READ(5,505) HD1,HD2
   42 IF((IST+NFT-NLV).GT.0) GO TO 130
      IDGF=NFT+NHDA-4
      XDGF=IDGF
      NJ=NFT-2
      DO 44 I=1,NFT
      Y(I)=E(IST+I)
   44 X(I)=VF(IST+I)
      IF(IWRST.GT.0) GO TO 46
   45 WRITE(6,601) (TITL(I),I=1,16),ERY,NISOT,(BZ(I),I=1,NISOT)
      IF(ISH.GT.0) WRITE(6,618) (J,SH(J),J=2,NISOT)
      IF((NISOT.GT.1).AND.(ISH.LE.0)) WRITE(6,617) (J,SH(J),DSH(J),J=2,
     1 NISOT)
   46 IWRST=0
      IF(NHD.EQ.0) GO TO 60
      IF(NHD.EQ.-1) GO TO 54
      ZN=HD1
      WRITE(6,609) ZN
      IF(ABS(ZN-2.).LT.0.01) GO TO 84
      IF(NHD-1) 56,60,48
```

```
   48 CN=HD2
      WRITE(6,619)CN
      A1=1.+1./ZN
      A2=A1-0.5
C*** GAMMA  IS THE LIBRARY SUBROUTINE PRODUCING VALUES OF THE GAMMA
C    FUNCTION,  GM1=GAMMA(A1).   IN ERROR MODE EXITS TO STATEMENT 200.
      CALL GAMMA(A1,GM1,$50,$200)
   50 CALL GAMMA(A2,GM2,$52,$200)
   52 XKN=GM1*SQPI/(GM2*SBZ(1)) *2.*ZN*CN**(-1./ZN)
      GO TO 60
   54 D=HD1
      GO TO 58
   56 D=HD2
   58 WRITE(6,610) D
   60 IF(IDR2.LT.0) GO TO 78
      IF(NFT.LE.3) GO TO 78
      NU=3
      CALL PLYFIT(NFT,NU,NUB,AA,ERY,IDR2)
      WRITE(6,603)NU
      IF(IDR2.LE.0) GO TO 78
      CALL UD2DV2(NFT,NJ,NHD,IDGF,ZN,VD,D,XKN,ER2)
      GO TO 80
   78 CALL UD1DV1(NFT,NJ,NHD,IDGF,ZN,VD,D,XKN,ER2,IDR2)
   80 IF(ER2.LT.0.) GO TO 112
      IF(ABS(ZN-2.).GT.0.01) GO TO 90
   84 CALL ZNEQ2(ZN,NFT,NJ,D,DD,CN,DCN,BZ(1),R2,ER2)
      DVD=0.
      DZN=0.
      VD=0.99E+30
      GO TO 106
   90 IF(NHD.EQ.2) GO TO 102
      A1=1.+1./ZN
      A2=A1-0.5
      CALL GAMMA(A1,GM1,$100,$200)
  100 CALL GAMMA(A2,GM2,$102,$200)
  102 CN=2.*ZN*SQPI/SBZ(1) *GM1/GM2
      CN=CN/XKN
      PW1=1./ZN
      DO 104 I=1,NFT
  104 R2(I)=CN/ABS(Y(I)-D)**PW1
      FC=-0.99E-31
      IF((ZN*ALOG10(CN)).LE.30.) FC=CN**ZN
      CN=FC
      DD=0.0
      DZN=0.0
      DCN=0.0
      DVD=0.0
      IF(IDGF.LE.0) GO TO 106
      CALL CONFID(ER2,NFT,IDGF,NHD,ZN,DZN,XKN,CN,DCN,VD,DVD,D,DD)
  106 CNU=CN+DCN
      CNL=CN-DCN
      ZNU=ZN+DZN
      ZNL=ZN-DZN
      VDU=VD+DVD
      VDL=VD-DVD
```

```
      DU=D+DD
      DL=D-DD
      WRITE(6,604) NFT,ER2,IDGF,D,ZN,VD,CN,DD,DZN,DVD,DCN,DU,ZNU,VDU,
     1  CNU,DL,ZNL,VDL,CNL
      DSH(1)=D
      VDIS(1)=VD
      IF(NISOT.LE.1) GO TO 112
      DO 110 J=2,NISOT
      VDIS(J)=VD/FMU(J)
  110 DSH(J)=SH(J)
      WRITE(6,615) NISOT,(BZ(J),FMU(J),SH(J),VDIS(J),J=1,NISOT)
  112 WRITE(6,605)
      NLB=1
      NK=NFT
      WRITE(6,606) (X(I),Y(I),X2(I),DY2(I),R2(I),I=1,NLB)
      WRITE(6,608) (X(I+NLB),Y(I+NLB),DG(I),D2G(I),RAT(I),DY1(I),
     1  X2(I+NLB),DY2(I+NLB),R2(I+NLB),I=1,NJ)
      IF((NJ+1).GE.NFT) GO TO 114
      WRITE(6,606) (X(I),Y(I),X2(I),DY2(I),R2(I),I=NK,NFT)
C*** PUNCH TRIAL PARAMETER VALUES AND FIT-CONTROLLING CONSTANTS FOR
C    INPUT TO GENERAL NON-LINEAR REGRESSION PROGRAM.
  114 PUNCH 501 , NFT,IST,NHD,ISH
      PUNCH 505, ZN,CN,(VDIS(J),J=1,NISOT),(DSH(J),J=1,NISOT)
      IF(NDT) 122,130,124
  122 NFT=NFT+NDT
      NUB=NU
      IF(NFT-3) 130,126,42
  126 IF(NHD.EQ.0) GO TO 130
      NJ=NFT-1
      GO TO 45
  124 IST=IST+NDT
      GO TO 42
  130 IF(ICAS-NCAS) 38,2,2
  200 ZN=1./(A1-1.)
      WRITE(6,607) ZN,A1,A2
      GO TO 130
  999 STOP
  501 FORMAT(20I4)
  502 FORMAT(16A5/10I4)
  503 FORMAT(8F10.3)
  504 FORMAT(5(F5.1,F10.3))
  505 FORMAT(F10.4,E10.5,6F10.3)
  601 FORMAT(1H1 /10X 16A5/1H0 2X 76HTHROUGHOUT, UNCERTAINTIES IN PARAME
     1TERS REPRESENT A 95/100 CONFIDENCE LIMIT.   /1H0 2X 105HSUCCESSIVE
     2 POLYNOMIAL FITS ASSUMED CONVERGED IF STANDARD ERROR HAS RELATIVE
     3DECREASE OF LESS THAN  5/100,  /20X 65HOR STANDARD ERROR IS LESS T
     4HAN THE PRECISION OF THE DATA,    ERY = F7.4/1H0 2X 12HFIT DATA FOR
     5  I2,35H ISOTOPIC SPECIES WITH  BZ VALUE(S)  4E14.7 )
  603 FORMAT(1H0 2X 16HINTERPOLATE WITH I3, 21H ORDER POLYNOMIAL FIT )
  604 FORMAT(1H0/3X 8HCONSIDER I3,29H LEVELS.  E FIT HAS  STDERR = E9.3,
     1  12H  FOR  IDGF= I3/ 1H0 5X 16HOBTAIN CONSTANTS 5X
     2  3HD = F10.3,5X 4HZN = F8.3,5X 4HVD = F7.3,5X 4HCN = E11.5/1H0 6X
     3 18HWITH UNCERTAINTIES 5X F10.3,9X F8.3,9X F7.3,9X E11.5/
     4    13X 12HUPPER BOUNDS 5X F10.3,9X F8.3,9X F7.3,9X E11.5/
     5    13X 12HLOWER BOUNDS 5X F10.3,9X F8.3,9X F7.3,9X E11.5 )
  605 FORMAT(1H0/6X 1HV    8X 1HE 9X 5HDG/DV 5X 7HD2G/DV2 6X 2HY1 7X
```

```
     1  5HDIFF1 4X 10H(VD-V)**PW 4X 5HDIFF2 8X 2HR2 )
 606 FORMAT(F9.2,E12.6,42X E13.5,E11.5,F9.4)
 607 FORMAT(1H0/10X 24HERROR.....IN GAMMA.  ZN=,E11.5,6H,  A1=,E11.5,
     1  6H,  A2=,E11.5)
 608 FORMAT(F9.2,E12.6,2E11.5,2E10.4,E13.5,E11.5,F9.4)
 609 FORMAT(1H0  2X 15HCONSTRAIN   N = F6.2)
 610 FORMAT(1H0  2X 18HCONSTRAIN  DISOC = F10.3)
 613 FORMAT(F10.4,E10.4,6F10.3)
 615 FORMAT(1H0/ 3X 31HABOVE VALUES ARE FOR ISOTOPE-1. 2X 7HFOR THE I2,
     1  22H ISOTOPIC SPECIES HAVE 13X2HBZ 10X 3HFMU 7X 2HSH 5X 2HVD/
     2  (72X E15.7,F11.7,F7.3,F8.3) )
 616 FORMAT(1H0 2X 21HSMOOTH DATA FOR FIRST I3,17H ISOTOPE(S) USING I2,
     1  20H-TH ORDER POLYNOMIAL  )
 617 FORMAT(1H0 2X 28HDETERMINE ISOTOPE SHIFT  SH( I2,3H) = F7.3,
     1  24H, WITH UNCERTAINTY  DSH= F6.3/)
 618 FORMAT(1H0 2X 28HHOLD ISOTOPE SHIFTS FIXED AT 4(7H    SH( I2,3H) =
     1    F7.3 ) )
 619 FORMAT(1H0  2X 15HCONSTRAIN  CN = E13.7)
      END
```

```
      SUBROUTINE UD1DV1(NFT,NJ,NHD,IDGF,ZN,VD,D,XKN,ER2,IDR2)
C*** SUBROUTINE TO FIT DATA USING SOME OF EQS.(5-7, AND A1-A4) FROM
C   REPORT  WIS-TCI-369(1970).  USES AT MOST 1-ST DERIVATIVE OF ENERGY
C   WITH RESPECT TO  V.  THIS APPROACH MAY ONLY BE USED IF (NHD.NE.0).
      COMMON/BLK1/T(50),X(50),Y(50),DG(50),D2G(50),RAT(50),DY1(50),
     1  DY2(50),X2(50),W(50)
      DIMENSION  VB(2),DVB(2)
      IO=0
      NU=1
      IADD=0
      XDGF=IDGF
      DO 2 I=1,NFT
    2 D2G(I)=0.0
      IF(NHD.GT.-2) GO TO 10
C*** IF  N AND  D BOTH FIXED, OBTAIN VALUES OF  VD AND  KN HERE.
      PW=2.*ZN/(ZN-2.)
      PW1=1./PW
      DO 6  I=1,NFT
      RAT(I)=(D-Y(I))**PW1
    6 DG(I)=0.0
```

```
      CALL FORSYT(X,RAT,W,NFT,VB,DVB,NU,DY1,IO,FPR,ER1,IADD)
      VD=-VB(1)/VB(2)
      XKN=ABS(VB(2)*PW)
      WRITE(6,606) ER1
      IF(VB(2).GE.0.) GO TO 32
      SM2=0.0
      DO 8 I=1,NFT
      DY2(I)=D-(VB(1)+VB(2)*X(I))**PW - Y(I)
    8 SM2=SM2+DY2(I)**2
      ER2=SQRT(SM2)
      IF(NFT.GT.2) ER2=ER2/SQRT(XDGF)
      GO TO 50
   10 IF(IDR2.EQ.0) GO TO 12
      DO 11 I=1,NJ
   11 DG(I)=0.5*(Y(I)-Y(I+2))
      WRITE(6,608)
   12 IF(NHD.LT.0) GO TO 22
      P = 2.*ZN/(ZN+2.)
      P1=1./P
      IF(NHD.EQ.2) GO TO 16
C***  IF   N   HELD FIXED, FIT HERE TO GET   D   AND   KN.
      DO 14 I=1,NJ
      DY2(I)=Y(I+1)
   14 RAT(I)=DG(I)**P
      CALL FORSYT(DY2,RAT,W,NJ,VB,DVB,NU,DY1,IO,FPR,ER1,IADD)
      XKN=ABS(VB(2))**P1
      D=-VB(1)/VB(2)
      WRITE(6,601) D,XKN,ER1
      IF(VB(2).GE.0.) GO TO 32
      GO TO 30
C***  IF BOTH  N  AND  CN  HELD FIXED, FIT HERE TO GET  D.
   16 D=0.0
      DO 18 I=1,NJ
   18 D=D+Y(I+1)+(DG(I)/XKN)**P
      D=D/NJ
      WRITE(6,603) D,ER1
      GO TO 30
C***  IF   D   HELD FIXED, FIT HERE TO GET   N   AND   KN.
   22 DO 24 I=1,NJ
      RAT(I)=LOG(DG(I))
   24 D2G(I)=LOG(D-Y(I+1))
      CALL FORSYT(D2G,RAT,W,NJ,VB,DVB,NU,DY1,IO,FPR,ER1,IADD)
      ZN=1./(VB(2)-0.5)
      WRITE(6,604) ZN,ER1
      IF(ABS(ZN-2.).LT.0.01) GO TO 999
      XKN=EXP(VB(1))
   30 IF((D.GT.Y(1)).AND.(D.GT.Y(NFT)).AND.(ZN.GT.0.)) GO TO 34
   32 WRITE(6,602)  ZN,D,XKN
      ER2=-1.
      GO TO 50
C***  KNOWING  N,  D,  AND  KN,  FIT TO GET  VD.
   34 PW=2.*ZN/(ZN-2.)
      PW1=1./PW
      HN=PW1*XKN
      HN1=1./HN
      VD=0.0
```

```
      DO 36 I=1,NFT
   36 VD=VD+X(I)+(D-Y(I))**PW1 *HN1
      VD=VD/NFT
      WRITE(6,605) VD
      IF((VD.LT.X(1)).OR.(VD.LT.X(NFT))) GO TO 32
      SM=0.0
      DO 38 I=1,NFT
      DY2(I)=D-(HN*(VD-X(I)))**PW - Y(I)
   38 SM=SM+DY2(I)
      DD=0.0
      IF(NHD.LT.0.) GO TO 40
      DD=SM/NFT
      D=D-DD
      WRITE(6,607) DD
   40 SM=0.0
      DO 42 I=1,NFT
      DY2(I)=DY2(I)-DD
   42 SM=SM+DY2(I)**2
      ER2=SQRT(SM)
      IF(IDGF.GT.0) ER2=ER2/SQRT(IDGF)
   50 DO 52 I=1,NFT
   52 X2(I)=ABS(VD-X(I))**PW
  999 RETURN
  601 FORMAT(1H0/3X 12HOBTAIN   D = F10.3,13H   AND   KN = E10.5, 68H
     1FROM A FIT TO     (DG/DV)**(2*N/(N+2)) = (D-E(V))*KN**(2*N/(N+2))
     2    /65X 16HHAVING   STDERR = E10.4 )
  602 FORMAT(1H0 10X 26HERROR *** FIT GIVES   ZN = F8.3,5X 3HD = F10.2,
     1  5X 4HKN = E10.5 )
  603 FORMAT(1H0/3X  12HOBTAIN   D = F10.3, 77H   FROM AVERAGE OF      D
     1= E(V) + ((DG/DV)/KN)**(2*N/(N+2)) .   HAS  STDERR = E10.4)
  604 FORMAT(1H0/3X  12HOBTAIN   N = F8.3, 94H   AND  KN  FROM A FIT TO
     1     LOG(DG/DV) = LOG(KN) + (.5+1/N)*LOG(D-E(V)) ,   HAVING  STDERR
     2 = E10.4 )
  605 FORMAT(1H0 2X 13HOBTAIN   VD = F8.3, 62H  AS AN AVERAGE OF      VD
     1= V + (1/HN)*(D-E(V))**((N-2)/(2*N))   )
  606 FORMAT(1H0/3X  98HOBTAIN  KN  AND  VD  FROM FIT TO      (D-E(V))**(
     1(N-2)/(2*N)) = (HN*VD) - HN*V ,   HAVING  STDERR = E10.4)
  607 FORMAT(12X 32HAND IMPROVEMENT IN  D  OF   DD =  F8.3)
  608 FORMAT(1H0/3X 72HAPPROXIMATE FIRST DERIVATIVE   DE(V)/DV   WITH
     1BY   (E(V+1)-E(V-1))/2.  )
      END
```

```
      SUBROUTINE UD2DV2(NFT,NJ,NHD,IDGF,ZN,VD,D,XKN,ER2)
C*** SUBROUTINE TO FIT DATA USING EQS.(15-16) FROM J.CHEM.PHYS.,
C   VOL.52,3869(1970). UTILIZES BOTH 1-ST AND 2-ND DERIVATIVES OF
C   ENERGY WITH RESPECT TO  V.
      COMMON/BLK1/T(50),X(50),Y(50),DG(50),D2G(50),RAT(50),DY1(50),
     1  DY2(50),X2(50),W(50)
      DIMENSION  VB(2),DVB(2)
      DOUBLE PRECISION  A(2,2),DT
      IO=0
      NU=1
      IADD=0
      XDGF=IDGF
      IF((NHD.EQ.-1).OR.(NHD.EQ.0)) GO TO 10
C** FIT TO GET  VD  HERE IF  N  IS HELD FIXED AT THE VALUE READ IN.
      VB(2)=(ZN-2.)/(ZN+2.)
      SM=0.0
      DO 4  I=1,NJ
      DY1(I)=RAT(I)-VB(2)*X2(I)
    4 SM=SM+DY1(I)
      VB(1)=SM/NJ
      SM2=0.0
      DO 6  I=1,NJ
      DY1(I)=VB(1)-DY1(I)
    6 SM2=SM2+DY1(I)**2
      ER1=SQRT(SM2/(NJ-1.))
      DVB(1)=T(NJ-1)*ER1/SQRT(FLOAT(NJ))
      DVB(2)=0.0
      VD=-VB(1)/VB(2)
      DVD=DVB(1)/VB(2)
      DZN=0.0
      GO TO 16
C** FIT TO GET  ZN AND  VD  HERE IF NEITHER IS HELD FIXED.
   10 CALL FORSYT(X2,RAT,W,NJ,VB,DVB,NU,DY1,IO,FPR,ER1,IADD)
      DVB(1)=DVB(1)*T(NJ-2)
      DVB(2)=DVB(2)*T(NJ-2)
      ZN=2.*(1.+VB(2))/(1.-VB(2))
      VD=-VB(1)/VB(2)
C*** CALCULATE  95/100  CONFIDENCE INTERVALS ON  N  AND  VD.
      SM1=0.0
      SM2=0.0
      DO 12 I=1,NJ
      DF=VD-X2(I)
      SM1=SM1+DF
   12 SM2=SM2+DF**2
      FERR=ER1*T(NJ-2)
      A(1,1)=NJ*VB(2)**2
      A(2,2)=16.*SM2/(ZN+2.)**4
      A(1,2)=4.*SM1*VB(2)/(ZN+2.)**2
      A(2,1)=A(1,2)
      NDM=2
      CALL DMTINV(A,NDM,NDM,DT,IER)
      IF((A(1,1).LE.0.D+0).OR.(A(2,2).LE.0.D+0)) WRITE(6,614) A(1,1),
     1  A(1,2),A(2,1),A(2,2)
      DVD=FERR*DSQRT(DABS(A(2,2)))
      DZN=FERR*DSQRT(DABS(A(1,1)))
   16 WRITE(6,612) NJ,ER1,VB(1),DVB(1),VB(2),DVB(2),ZN,DZN,VD,DVD
```

```
      IF(ABS(ZN-2.).LT.0.001) GO TO 999
      TST=(VD-X(1))*(ZN-2.)
      IF((TST.GT.0.).AND.(ZN.GT.0.)) GO TO 18
      WRITE(6,611)  ZN,VD
      ER2=-1.
      GO TO 999
   18 PW=2.*ZN/(ZN-2.)
      PW1=1./PW
      FZN2=1.
      IF(ZN.LT.2.0) FZN2=-1.
      DO 20 I=1,NFT
   20 X2(I)= (FZN2*(VD-X(I)))**PW
      IF(NHD.EQ.2) GO TO 30
      IF(NHD.GE.0) GO TO 40
C** FIT TO GET  CN  HERE IF  D IS CONSTRAINED TO THE VALUE READ IN.
      SM1=0.0
      SM2=0.0
      DO 22 I=1,NFT
      SM1=SM1+(Y(I)-D)*X2(I)
   22 SM2=SM2+X2(I)*X2(I)
      VB(2)=SM1/SM2
      SM2=0.0
      DO 26 I=1,NFT
      DY2(I)=D+VB(2)*X2(I)-Y(I)
   26 SM2=SM2+DY2(I)**2
      ER2=SQRT(SM2/XDGF)
      GO TO 50
C*** FIT TO GET  D IF  CN IS CONSTRAINED TO VALUE READ IN.
   30 VB(2)=-ABS(PW1*XKN)**PW
      D=0.0
      DO 34  I=1,NFT
      DY2(I)=Y(I)-VB(2)*X2(I)
   34 D=D+DY2(I)
      D=D/NFT
      SM2=0.0
      DO 36  I=1,NFT
      DY2(I)=D-DY2(I)
   36 SM2=SM2+DY2(I)**2
      ER2=SQRT(SM2/XDGF)
      GO TO 999
C** FIT TO GET  D  AND  CN  HERE IF NEITHER IS CONSTRAINED.
   40 CALL FORSYT(X2,Y,W,NFT,VB,DVB,NU,DY2,IO,FPR,ER2,IADD)
      IF(IDGF.GT.0) ER2=ER2*SQRT(FLOAT(NFT-2)/XDGF)
      D=VB(1)
   50 XKN=ABS(VB(2))**PW1*ABS(PW)
  999 RETURN
  611 FORMAT(1H0/1H0 5X 22HERROR ***** GET   ZN = E10.4, 12H,  AND  VD =
     1  E10.4 )
  612 FORMAT(1H0/ 3X 33HFIT TO  (D1G/DV1)/(D2G/DV2)  WITH I3,20H LEVELS
     1HAS STDERR = E9.3/ 3X 16HAND YIELDS  AI = E11.5,1H( E9.4,
     2  8H)    SL = F8.4,1H( F7.4,8H)    ZN = F8.4,1H( F7.4,8H)    VD =
     3  F7.3,1H( F6.3,1H) )
  614 FORMAT(1H0/10X 27HERROR *** MATRIX INVERSE IS 2D14.7/(37X 2D14.7))
      END
```

```
      SUBROUTINE ZNEQ2(ZN,NFT,NJ,D,DD,CN,DCN,BZ,R2,ER2)
C***  ESTIMATE PARAMETER VALUES OF  D AND KN  IF N=2
      DOUBLE PRECISION  A(2,2),DT
      DIMENSION  R2(50),VB(2),DVB(2)
      COMMON/BLK1/T(50),X(50),Y(50),DG(50),D2G(50),RAT(50),DY1(50),
     1  DY2(50),X2(50),W(50)
      IADD=0
      IO=0
      NU=1
      ZN=2
      DO 2  I=1,NJ
      D2G(I)=0.0
      DY2(I)=Y(I+1)
    2 RAT(I)=0.0
      CALL FORSYT(DY2,DG,W,NJ,VB,DVB,NU,DY1,IO,FPR,ER1,IADD)
      WRITE(6,601) ER1
      D=-VB(1)/VB(2)
      XKN=VB(2)
      SM1=0.0
      DY2(1)=0.0
      DO 4  I=2,NFT
      DY2(I)=Y(I)-D+(D-Y(1))*EXP(-XKN*(X(I)-X(1)))
    4 SM1=SM1+DY2(I)
      SM1=SM1/NFT
      SM2=0.0
      DO 6  I=1,NFT
      DY2(I)=SM1-DY2(I)
    6 SM2=SM2+DY2(I)**2
      ER2=SQRT(SM2)
      IF(NFT.GT.2) ER2=ER2/SQRT(FLOAT(NFT-2))
      FERR=ER2*T(NFT-2)
      CN=(6.2831852/XKN)**2/BZ
      FCT=-0.5*XKN/CN
      A(1,2)=0.0
      A(2,2)=0.0
      DO 8  I=1,NFT
      R2(I)=SQRT(CN/(D-Y(I)))
      DD=(D-Y(I))*X(I)*FCT
      A(1,2)=A(1,2)+DD
    8 A(2,2)=A(2,2)+DD**2
      A(2,1)=A(1,2)
      A(1,1)=NFT
      NDM=2
      CALL DMTINV(A,NDM,NDM,DT,IER)
      DD=FERR*DSQRT(DABS(A(1,1)))
      DCN=FERR*DSQRT(DABS(A(2,2)))
  999 RETURN
  601 FORMAT(1H0/5X 104HSINCE  N = 2 , OBTAIN VALUES OF  D  AND  KN  FR
     1OM A FIT TO     DG/DV = KN*(D-E(V)) ,   HAVING  STDERR = E9.4 )
      END
```

```
      SUBROUTINE PLYFIT(NFT,NN,NUB,AA,ERY,IDR2)
C*** FIT POLYNOMIALS OF INCREASING ORDER TO THE DATA TILL STANDARD ERROR
C    EITHER CONVERGES, OR BECOMES LESS THAN   ERY.
C*** IF(IDR2.EQ.0) CALCULATE 1-ST DERIVATIVES, DG.  IF(IDR2.GT.0)
C    CALCULATE BOTH 1-ST AND 2-ND DERIVATIVES, DG AND D2G.  IF(IDR2.LT.0)
C    CALCULATE NO DERIVATIVES.
      COMMON/BLK1/T(50),X(50),Y(50),DG(50),D2G(50),RAT(50),DY1(50),
     1 DY2(50),X2(50),W(50)
      DIMENSION  AA(11),VB(11),DVB(11)
      IO=0
      IADD=0
      WRITE(6,601) X(1),Y(1)
      DO 10 I=1,NFT
      DG(I)=Y(I)-Y(1)
   10 X2(I)=X(I)-X(1)
    2 NU=NN
      CALL FORSYT(X2,DG,W,NFT,VB,DVB,NU,DY1,IO,FPRTL,ERR,IADD)
      IADD=1
      NN=NU+1
      FTST=FPRTL-T(NFT-NN)**2
      WRITE(6,602) NU,NFT,ERR,FTST,(VB(I),I=1,NN)
      IF(NU.LE.3) GO TO 4
C*** IF THE DECREASE IN THE SUM OF SQUARES OF RESIDUALS ON GOING FROM
C    AN (M-1)-TH DEGREE FIT TO A  M-TH DEGREE FIT IS SIGNIFICANT AT THE
C    95/100 CONFIDENCE LIMIT LEVEL, THEN  (FTST.GT.0)
      IF(FTST.LT.0) GO TO 8
    4 DO 6  I=1,NN
    6 AA(I)=VB(I)
      IF((NN.LT.NFT).AND.(NU.LT.NUB).AND.(ERR.GT.ERY)) GO TO 2
      NU=NU+1
    8 NN=NU-1
      IF(IDR2.LT.0) GO TO 999
C*** CALCULATE FIRST DERIVATIVES EXCEPT FOR BOTTOM AND TOPMOST LEVELS.
      NF1=NFT-1
      K=NN+1
      DO 64 J=1,NN
      K=K-1
      DY1(J)=K*AA(K+1)
   64 DY2(J)=(K-1)*DY1(J)
      NJ=0
      DO 68 I=2,NF1
      NJ=NJ+1
      D1=DY1(1)
      DO 66 J=2,NN
   66 D1=X2(I)*D1+DY1(J)
   68 DG(NJ)=D1
      IF(IDR2.LE.0) GO TO 78
C*** NOW CALCULATE 2-ND DERIVATIVES.
      K=NN-1
      DO 72 I=2,NF1
      IJ=I-1
      D2=DY2(1)
      DO 70 J=2,K
   70 D2=X2(I)*D2+DY2(J)
      D2G(IJ)=D2
```

```
   72 RAT(IJ)=DG(IJ)/D2G(IJ)
   78 DO 80 I=1,NJ
   80 X2(I)=X(I+1)
  999 RETURN
  601 FORMAT(1H0/3X 69HFOR SMOOTHING POLYNOMIAL FIT, SCALE  X  AND  Y  V
     1ALUES BY SUBTRACTING  E13.7,4H AND E13.7, 16H , RESPECTIVELY.  )
  602 FORMAT(1H0 5X 26HLEAST SQUARES FIT OF ORDER,I3,3H TO,I3,
     1  30H BINDING ENERGIES HAS  STDERR= ,E10.4,14H,     F-TEST = E9.4/
     2  6X 23HAND YIELDS COEFFICIENTS 5X 7E14.7/( 15X 8E14.7))
      END
```

```
      SUBROUTINE FORSYT (X,Y,W,N,C,E,M,XDF,IO,FPRTL,MSR,IADD)
C*** SUBROUTINE TO PERFORM LEAST-SQUARES POLYNOMIAL FITTING USING
C   ORTHOGONAL POLYNOMIALS, BY A METHOD OF FORSYTHE.
C      W(I) -- WEIGHT ASSIGNED TO ORDERED PAIR X(I),Y(I)
C     N -- NO. OF DATA POINTS
C     C -- COEFFICIENTS OF SINGLE POLYNOMIAL IN X
C     E - ERROR VECTOR FOR C
C     M -- DEGREE OF POLYNOMIAL TO BE FITTED
C     IO - IF = 0, NO PRINTING. IF = 1 PRINTING
C*** XDF - RESIDUALS.
C*** FPRTL  IS THE PARTIAL F-TEST FOR THE FIT.  FPRTL=(IMPROVEMENT IN
C   SUM OF SQUARES OF RESIDUALS)/(ROOT MEAN SQUARE OF RESIDUALS)
C*** MSR - ROOT MEAN SQUARE RESIDUAL.
C*** ON FIRST ENTRY WITH A GIVEN SET OF DATA ALWAYS SET  IADD=0.
C*** IF(IADD.GT.0) USE OPTION FOR ADDING ONE HIGHER DEGREE TO A POLYNOMIA
C   PREVIOUSLY FITTED TO THE SAME DATA.
C*** SUBROUTINE WRITTEN AND TESTED BY R.A. LA BUDDE.
      DIMENSION  X(N),Y(N),W(N),C(11),E(11),U(11),V(11),A(11),B(11,11),
     1  D(11),XDF(N)
      IMPLICIT DOUBLE PRECISION (A-H,O-W)
      REAL FPRTL,MSR,W,C,E
      MM = M + 1
      IF(IADD.LE.0) GO TO 4
      ILO=MM
      GO TO 500
    4 ILO=2
      DO 8 I=1,10
      II = I + 1
      DO 6 J=1,II
    6 B(I,J) = 0.D0
```

```
      B(11,I) = 0.D0
    8 B(I,I) = 1.D0
      B(11,11) = 1.D0
      V(1) = 0.D0
      U(1) = 0.D0
      A(1) = 0.D0
      D(1) = 0.D0
      VY = 0.D0
      DO 300 I = 1,N
      T = DBLE(W(I))
      D(1) = D(1) + T
      A(1) = A(1) + T*DBLE(Y(I))
      U (1) = U(1) + T*DBLE(X(I))
300   VY = VY + T*DBLE(Y(I))*DBLE(Y(I))
      A(1) = A(1)/D(1)
      U(1) = U(1)/D(1)
      B(2,1) = - U(1)
      AYY = 0.D0
      VY = VY - A(1)*A(1)*D(1)
500   DO 1000 I = ILO,MM
      II = I - 1
      U(I) = 0.D0
      A(I) = 0.D0
      D(I) = 0.D0
      V(I) = 0.D0
      DO 800 J = 1,N
      P1 = 1.D0
      P2 = 0.D0
      WORK = DBLE(X(J))
      DO 700 K = 1,II
      T = (WORK -U(K))*P1 - V(K)*P2
      P2 = P1
700   P1 = T
      T = DBLE(W(J))*P1
      U(I) = U(I) + T*P1*WORK
      V(I) = V(I) + T*P2*WORK
      D(I) = D(I) + P1*T
800   A(I) = A(I) + T*DBLE(Y(J))
      U(I) = U(I)/D(I)
      V(I) = V(I)/D(II)
      A(I) = A(I)/D(I)
      WAYY = A(I)*A(I) *D(I)
      AYY = AYY + WAYY
      IF (I.EQ.2) GO TO 1000
      B(I,1) = -U(II)*B(II,1) - V(II)*B(I-2,1)
      DO 900 J = 2,II
900   B(I,J) = B(II,J-1) - U(II)*B(II,J) - V(II)*B(I-2,J)
1000  CONTINUE
      IF(IO.LE.0) GO TO 28
      WRITE(6,604)
      WRITE(6,602)
      DO 26 I=1,MM
   26 WRITE(6,601) (B(I,J),J=1,MM)
      WRITE(6,605)
   28 SYN = DBLE(N)*(VY - AYY)/D(1)
```

```
      IF(N.GT.MM) SYN=SYN/DBLE(FLOAT(N-MM))
      DO 2000 K = 1,MM
      T = 0.D0
      WORK = 0.D0
      DC 1500 J = K,MM
      T = T + A(J)*B(J,K)
 1500 WORK = WORK + B(J,K)*B(J,K)/D(J)
      IF(IO.GT.0) WRITE(6,603) K,T
      C(K) = T
 2000 E(K)=DSQRT(DABS(SYN*WORK))
      FP=DBLE(N)*WAYY/(SYN*D(1))
      IF(IO.LE.0) GO TO 4000
C*** WRITE OPTION FOR (IO.GT.0)
      P1 = DBLE(N)*AYY/(DBLE(M)*SYN*D(1))
      WORK = AYY/VY
      T=DSQRT(DABS(SYN))
      WRITE (6,10) VY,SYN,T
      T = DSQRT(WORK)
      WRITE (6,20) P1,FP,WORK,T
      WRITE (6,30)
      IF (ILO.GT. 2) GO TO 2500
      I = 0
      T=DSQRT(ABS(SYN/D(1)))
      WRITE (6,40) I,D(1),A(1),T
2500  DO 3000 I = ILO,MM
      II = I - 1
      T=DSQRT(ABS(SYN/D(I)))
3000  WRITE (6,40) II,D(I),A(I),T,U(II),V(II)
      WRITE(6,604)
 4000 MSR=0.0
      DO 44 I=1,M
      L=M+1
      Z=C(M+1)
      DO 42 J=1,M
   42 Z=Z*X(I)+C(L-J)
      XDF(I)=Z-Y(I)
   44 MSR=MSR+XDF(I)**2
      IF(N.GT.MM) MSR=SQRT(MSR/FLOAT(N-MM))
      FPRTL=FLOAT(N)*WAYY/(D(1)*MSR**2)
3500  RETURN
10    FORMAT ('0TOTAL SUM OF SQUARES',D15.6,5X,'MEAN SQUARE RESIDUAL',D1
     15.6,5X,'RMS RESIDUAL',D15.6)
20    FORMAT ('0TOTAL F-VALUE',D15.6,5X,'PARTIAL F-VALUE',D15.6/5X,
     1'COEFFICIENT OF DETERMINATION',D15.6,5X,'MULTIPLE CORRELATION CONS
     2TANT',D15.6)
   30 FORMAT ('0POLYNOMIAL',2X,'NORMALIZATION',4X,'COEFFICIENT',7X,'ERRO
     1R', 9X,'RECURSION' )
   40 FORMAT(5X I6, 5D15.7 )
  601 FORMAT(9D13.6)
  602 FORMAT(1H0 5X 10HB-ARRAY IS  /)
  603 FORMAT( 5X 8HFOR  K = I3,6X 'COEFFICIENT =' D15.8 )
  604 FORMAT(/1X,110(1H*))
  605 FORMAT(1H0 1X)
      END
```

```
      SUBROUTINE CONFID(ER2,NFT,IDGF,NHD,ZN,DZN,XKN,CN,DCN,VD,DVD,D,DD)
C*** SUBROUTINE TO CALCULATE  95 PERCENT CONFIDENCE LIMITS ON FITTED
C    PARAMETER VALUES. YIELDS RESULTS WHICH ARE APPROXIMATE IN TWO WAYS.
C    1-ST, HAVE NOT COMPLETELY OPTIMIZED THE PARAMETER VALUES, THOUGH ARE
C    PROBABLY VERY CLOSE. ***  2-ND, IMPLICITLY ASSUME THAT THE FUNCTION
C    IS LINEAR IN THE PARAMETERS IN AN INTERVAL ABOUT THE GIVEN VALUES.
      COMMON/BLK1/T(50),X(50),Y(50),DG(50),D2G(50),RAT(50),DY1(50),
     1  DY2(50),X2(50),W(50)
      DOUBLE PRECISION  A(4,4),ANM(4),DT,Z
      DIMENSION  DYDP(50,4),AH(4)
      FZN2=1.
      IF(ZN.LT.2) FZN2=-1.
      PW=2.*ZN/(ZN-2.)
      SL=-(ABS(XKN/PW))**PW
      NDIM=4
      L=2
      IF(NHD.EQ.-2) L=1
      IF(NHD.GT.0) L=L-NHD
      JJ=L+1
      IF(L.LE.0) GO TO 8
      FCT=SL/(CN*(0.5*ZN-1.))
      DO 6 I=1,NFT
    6 DYDP(I,L)=-FCT*X2(I)
    8 FCT=PW*SL
      DO 10 I=1,NFT
   10 DYDP(I,JJ)= FCT*X2(I)/(VD-X(I))
      IF(NHD.EQ.-2) GO TO 20
      IF(NHD.GT.0) GO TO 14
      XHN=XKN/PW
      DO 12 I=1,NFT
      DY=XHN*(VD-X(I))
   12 DYDP(I,1)=-ALOG(DY)*SL*X2(I)*4./(ZN-2.)**2
      IF(NHD.LT.0) GO TO 20
   14 KK=JJ+1
      DO 16 I=1,NFT
   16 DYDP(I,KK)=1.0
   20 NORD=4-ABS(NHD)
      DO 24 J=1,NORD
      DO 24 K=1,J
      Z=0.0D+000
      DO 22 I=1,NFT
   22 Z=Z+DBLE(DYDP(I,J))*DBLE(DYDP(I,K))
      A(J,K)= Z
   24 A(K,J)= Z
      DO 32 J=1,NORD
      ANM(J)=0.D+000
      DO 28 K=1,NORD
   28 ANM(J)=ANM(J)+DABS(A(J,K))
      DO 30 K=1,NORD
   30 A(J,K)=A(J,K)/ANM(J)
   32 AH(J)=A(J,J)
      CALL DMTINV(A,NORD,NDIM,DT,IER)
      DO 26 I=1,NORD
      TST=AH(I)*A(I,I)
      IF(ABS(TST).GT.0.1E+07) WRITE(6,603) I,TST
```

```
      IF(A(I,I).GT.0.D+000) GO TO 26
      WRITE(6,601) I,A(I,I)
      A(I,I)=-A(I,I)
   26 A(I,I)=A(I,I)/ANM(I)
      FERR=T(IDGF)*ER2
      DVD=FERR*DSQRT(A(JJ,JJ))
      DCN=0.0
      IF(NHD.LT.2) DCN=FERR*DSQRT(A(L,L))
      DZN=0.0
      IF(L.GT.1) DZN=FERR*DSQRT(A(1,1))
      DD=0.0
      IF(NHD.GE.0) DD=FERR*DSQRT(A(KK,KK))
   99 RETURN
  601 FORMAT(1H0 5X 18HERROR *** FOR  I = I2, 40H MATRIX INVERSE IN  CON
     1FID HAS  C(I,I) = D14.7)
  603 FORMAT(1H0 5X ,'CAUTION *** CONFIDENCE LIMITS POSSIBLY UNRELIABLE
     1SINCE FOR   I =' I2, '   FIND   A(I,I)*AINV(I,I) =' E10.5)
      END
```

```
      SUBROUTINE DMTINV(A,N,NDIM,DET,IER)
C*** SUBROUTINE TO INVERT MATRIX  A  BY METHOD OF GAUSS-JORDAN
C   ELIMINATION WITH PARTIAL PIVOTING. INVERSE IS RETURNED IN THE
C   INPUT MATRIX  A.  ** DIMENSION OF  A  IS (NDIM*NDIM), ALTHOUGH
C   THE MATRIX TO BE INVERTED IS ONLY (N*N).   ***  IER=1  IF MATRIX
C   IS SINGULAR TO THE PRECISION OF THE MACHINE, OTHERWISE  IER=0.
C ** DET  IS THE DETERMINANT OF INPUT  A. ** EVERYTHING DOUBLE PRECISION
C*** ROUTINE WRITTEN AND TESTED BY  R.A. LA BUDDE.
      DIMENSION A(1),ROW(100)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER ROW
      IER=0
      AU = 0.D0
      AL = 1.D+300
      DET = 1.D0
      NK = - NDIM
      DO 1000 K = 1,N
      NK = NK + NDIM
      KK = NK + K
      AMAX = A(KK)
      NI = K
      DO 200 I = K,N
      KI = NK + I
      IF (DABS(AMAX) .GE. DABS(A(KI))) GO TO 200
      AMAX = A(KI)
      NI = I
```

```
 200   CONTINUE
       DET = DET*AMAX
       IF (AL .GT. DABS(AMAX)) AL = DABS(AMAX)
       IF (AU .LT. DABS(AMAX)) AU = DABS (AMAX)
       PIVRAT = AL/AU
       IF (PIVRAT .GT. 1.D-12) GO TO 300
       WRITE (6,1) K,DET,PIVRAT
       IER=1
       RETURN
   300 ROW(K) = NI
       IF (NI .EQ. K) GO TO 350
       DET = - DET
       NI = NI - NDIM
       KI = K - NDIM
       DO 250 I = 1,N
       KI = KI + NDIM
       NI = NI + NDIM
       DODA = A(KI)
       A(KI) = A(NI)
 250   A(NI) = DODA
 350   NI = - NDIM
       DO 800 I = 1,N
       NI = NI + NDIM
       IF (I .EQ. K) GO TO 800
       KI = NI + K
       A(KI) = A(KI)/AMAX
       DO 700 J = 1,N
       IF (J .EQ. K ) GO TO 700
       JI = NI + J
       JK = NK + J
       A(JI) = A(JI) - A(JK)*A(KI)
 700   CONTINUE
 800   CONTINUE
       DO 900 I = 1,N
       KI = NK + I
 900   A(KI) = -A(KI)/AMAX
 1000  A(KK) = 1.D0/AMAX
       NK = - NDIM
       DO 1500 K = 1,N
       NK = NK + NDIM
       IF (ROW(K) .EQ. K) GO TO 1500
       NI = (ROW(K) - 1)*NDIM
       DO 1200 J = 1,N
       JK = NK + J
       JI = NI + J
       DODA = A(JK)
       A(JK) = A(JI)
 1200  A(JI) = DODA
 1500  CONTINUE
       RETURN
     1 FORMAT(/'0GJR FAILS AT STEP',I6,2X,'MATRIX IS SINGULAR TO PRECISIO
      1N OF MACHINE'/5X,'DETERMINANT',D20.10/5X,'RATIO OF MIN TO MAX PIVO
      2TS',D20.10)
       END
```

```
CHLORINE B-3PI(0+U) LEVELS OF  DOUGLAS, MOLLER, AND STOICHEFF.
   1   1   0
   0.01     1.036912
  19  31
  876.90     873.67     868.43     860.69     849.68     834.90     815.73     791.59
  762.08     726.59     684.78     636.20     580.18     516.38     444.19     363.28
  273.25     173.48      63.68
  19   0  -1   1  -1
   5.0
BROMINE B-3PI(0+U) LEVELS OF HORSLEY AND BARROW FOR (79,79) AND (81,81) ISOTOPES
   2   3   1
   0.01     2.34018   2.39944
 2.029
   4  53
  574.47     571.77     568.20     563.65
   4  53
  574.81     571.61     567.45     562.28
   8   0  -1   1   1
 5.0
   8   0  -1   1   1
 6.0
   8   0  -1   0   1
```

Appendix B: Nonlinear Least-Squares Fitting Program to Obtain Final Best Parameter Values

A Fortran V listing for the program used to perform the final fits to Eq. (4) is presented below. As input, it requires reasonably good initial trial parameter values (see Appendix A). Subroutine GASAUS, which was used to perform the least squares fitting, is a University of Wisconsin Computing Center library subroutine, and listings and documentation for it may be obtained from:

Information and Documentation Office
University of Wisconsin Computing Center
1210 West Dayton Street
Madison, Wisconsin 53706

```
C*** PROGRAM TO PERFORM NON-LINEAR LEAST-SQUARES FIT OF EXPERIMENTAL
C    VIBRATIONAL ENERGIES TO  LE ROY - BERNSTEIN  WKB-BASED EXPRESSION
C    FOR VIBRATIONAL ENERGIES OF HIGHLY EXCITED LEVELS.  PARAMETERS ARE
C    THE DISSOCIATION LIMIT  D, THE POWER  N  AND COEFFICIENT  CN  OF
C    THE EFFECTIVE LOCAL INVERSE-POWER POTENTIAL, AND THE INTEGRATION
C    CONSTANT  VD , WHICH FOR (N.GT.2) CORRESPONDS TO THE VIBRATIONAL
C    INDEX AT THE DISSOCIATION LIMIT. *** PROGRAM CAN CONCURRENTLY FIT
C    DATA FOR DIFFERENT ISOTOPES OF A GIVEN SPECIES, USING A COMMON  N
C    AND  CN, BUT INDEPENDENT VALUES OF  VD  AND  D.
C*** PROGRAM WRITTEN AND TESTED BY R.J. LE ROY.
      EXTERNAL  MODEL
      COMMON/BLK1/NISOT,NDSOC,X(50),FMU(4),ISOT(4),ZN,HN,VH(4),DSOC,
     1  SH(4),NHD,ESC
      DIMENSION  E(50),SCRAT(400),TITL(16),BDLW(9),BDUP(9),PAR(9),
     1  R2(50),G(50),VF(50),SBZ(4),BZ(4),DVD(4),DD(4),VD(4),DY(50)
      PI=3.1415926
      SQPI=SQRT(PI)
C*** CONSTANTS CONTROLLING NON-LINEAR LEAST-SQUARES SUBROUTINE  GASAUS,
C    WHICH TRIES UP TO  MXIT  TIMES TO CONVERGE.
      MXIT=50
      PRN=0.0
      BDFC=2.E+06
      EPS1=0.1E-07
      EPS2=0.1E-07
      EPS3=0.1E-07
      GMA=0.01
      FNU=10.
C*** TITL  IS THE NAME OF THE SYSTEM CONSIDERED.
C*** NISOT  IS THE NO. OF DIFFERENT ISOTOPIC MOLECULES CONSIDERED AT ONCE
C*** NCAS  IS THE NO. OF DIFFERENT FITS TO BE MADE TO THE DATA FOR
C    THIS SYSTEM.
    4 READ(5,503)  (TITL(I),I=1,16),NISOT,NCAS
C*** BZ  IS A NUMERICAL FACTOR FOR EACH ISOTOPIC MOLECULE, INCLUDING
      IF(NCAS.LE.0) GO TO 99
C    REDUCED MASS, ETC.   BZ=8*PI**2*MU(AMU)*1(1/CM)*(1.(ANGST))**2/H**2
      READ(5,502)  (BZ(I),I=1,NISOT)
      NLV=0
      DO 20 IS=1,NISOT
      SBZ(IS)=SQRT(BZ(IS))
      FMU(IS)=SBZ(1)/SBZ(IS)
C*** ISOT  IS THE NO. OF LEVELS USED FOR ISOTOPE (IS)
C*** IF(IVH.LT.0) READ IN ENERGIES AND VIB NUMBERING TOGETHER, OTHERWISE
C    READ ONLY ENERGIES AND NUMBER VIB LEVELS CONSECUTIVELY DOWN FROM
C    V=IVH  AS THE HIGHEST.  *** ALL ENERGIES IN WAVENUMBERS.
      READ(5,501) ISOT(IS),IVH
      NL1=NLV+1
      NLV=NLV+ISOT(IS)
C*** READ IN LEVEL ENERGIES, HIGHEST LEVELS FIRST.
      IF(IVH.LT.0) GO TO 14
      READ(5,502) (E(I),I=NL1,NLV)
      ISOTP=ISOT(IS)
      DO 12 I=1,ISOTP
   12 VF(NL1+I-1)=IVH+1-I
      GO TO 20
   14 READ(5,505) (VF(I),E(I),I=NL1,NLV)
```

```
   20 CONTINUE
      NPAR=2*(1+NISOT)
C*** ESC  IS AN ARBITRARY SCALING FACTOR SUBTRACTED FROM TRIAL  D.
      READ(5,502) ESC
      WRITE(6,601)  (TITL(I),I=1,16),NISOT  ,(BZ(J),J=1,NISOT)
      WRITE(6,610) ESC
      DO 90 ICAS=1,NCAS
C*** FIT THE FIRST  NFT  LEVELS, STARTING BELOW THE HIGHEST  ND1 OF THEM
C*** IF(NISOT.GT.1)  SET  ND1=0
C*** ABS(NHD) IS THE NO. OF PARAMETERS TO BE HELD FIXED AT THE TRIAL VALUES
C    IF(NHD.EQ.1) FIX ONLY  N.  *** IF(NHD.EQ.-1) FIX ONLY  D.
C*** IF(NHD.EQ.2) FIX N AND  CN.  IF(NHD.EQ.-2) FIX BOTH  N  AND  D.
C*** IF(ISH.GT.0) WHERE (NISOT.GT.1), SHIFT ENERGIES FOR DIFFERENT
C    ISOTOPES BY KNOWN INITIAL-STATE ISOTOPE SHIFTS.
      READ(5,501) NFT,ND1,NHD,ISH
      IF(ABS(NHD).GT.2) NHD=0
      IF(NHD.LT.0)  ISH=1
      NDSOC=1
      IF(ISH.LE.0) NDSOC=NISOT
C*** INITIAL TRIAL PARAMETER VALUES.  PAR(1)=N, PAR(2)=CN,
C    PAR(3,...,2+NISOT)=VD   FOR DIVERS ISOTOPES, PAR(3+NISOT)=D
C             FOR ISOTOPE 1, AND ALL OTHER PARAMETERS ARE ESTIMATES OF THE
C    ISOTOPE SHIFTS  SH(J) FOR ISOTOPES J=2,3, ETC., WHERE  SH(J) IS
C    SUBTRACTED FROM THE ENERGIES FOR ISOTOPE  J TO MAKE THEM CONSISTENT
C    WITH THOSE FOR  J=1.
C*** NOTE THAT IN THE ACTUAL FITTING USE  PAR(2)=HN
C    AND  PAR(3,4,...)=HN*VD(3,4,...)
      READ(5,504) (PAR(I),I=1,NPAR)
      CNN=PAR(2)
      A1=1.+1./PAR(1)
      A2=A1-0.5
      CALL GAMMA(A1,GM1,$24,$89)
   24 CALL GAMMA(A2,GM2,$26,$89)
   26 FCT=(PAR(1)-2.)*GM1/GM2 *SQPI/SBZ(1)
      PAR(2)=FCT*PAR(2)**(-1./PAR(1))
      DO 28 J=1,NISOT
   28 PAR(2+J)=PAR(2)*FMU(J)*PAR(2+J)
      PAR(3+NISOT)=PAR(3+NISOT)-ESC
      IF((ND1+NFT-NLV).GT.0) GO TO 90
C*** SELECT THE  NFT LEVELS TO BE FITTED.
      IF(NISOT.GT.1) GO TO 30
      ISOT(1)=NFT
      ISH=0
      NDSOC=1
      GO TO 42
   30 ND1=0
      IF(NLV.EQ.NFT) GO TO 42
      NDF=NLV-NFT
      DO 40 IDF=1,NDF
      ISMX=NISOT
      IMX=NLV
      VB=FMU(ISMX)*VF(IMX)
      JF=0
      DO 34 IS=1,NISOT
      JI=JF+1
      JF=JF+ISOT(IS)
```

```
      DO 34 I=J1,JF
      VTST=FMU(IS)*VF(I)
      IF(VTST.GE.VB) GO TO 34
      ISMX=IS
      IMX=I
      VB=VTST
   34 CONTINUE
      ISOT(ISMX)=ISOT(ISMX)-1
      IF(ISOT(ISMX).LE.0) NISOT=NISOT-1
      IF(IMX.EQ.NLV) GO TO 40
      IM1=IMX+1
      DO 36 I=IM1,NLV
      VF(I-1)=VF(I)
   36 E(I-1)=E(I)
   40 NLV=NLV-1
   42 DO 44 I=1,NFT
      X(I)=VF(ND1+I)
   44 G(I)=E(ND1+I)
C*** PREPARE PARAMETERS FOR FITTING.
      K=0
      NP=NPAR
      SH(1)=0.0
      IF(ISH.LE.0) GO TO 48
      DO 46 J=2,NISOT
   46 SH(J)=PAR(2+NISOT+J)
      NP=NPAR-NISOT+1
   48 ZN=PAR(1)
      HN=PAR(2)
      DSOC=PAR(3+NISOT)
      NP=NP-ABS(NHD)
      IF((NHD.EQ.-1).OR.(NHD.EQ.0)) GO TO 56
      K=NHD
      IF(NHD.EQ.-2) K=1
      DO 54 I=1,NP
   54 PAR(I)=PAR(I+K)
   56 DO 58 I=1,NP
      BDUP(I)=ABS(PAR(I)*BDFC)
   58 BDLW(I)=-BDUP(I)
C*** CALL NON-LINEAR LEAST-SQUARES FITTING SUBROUTINE.
      CALL GASAUS(PRN,MODEL,NFT,G,NP,PAR,BDUP,BDLW,EPS1,EPS2,EPS3,MXIT,
     1  GMA,FNU,SCRAT)
      WRITE(6,601)  (TITL(I),I=1,16),NISOT ,(BZ(J),J=1,NISOT)
      CALL MODEL(PAR,DY,NFT,NP)
      IF((NHD.GT.0).OR.(NHD.EQ.-2)) WRITE(6,608) ZN
      IF(NHD.EQ.2) WRITE(6,615) CNN
      DSPR=DSOC+ESC
      IF(NHD.LT.0) WRITE(6,609) DSPR
      IF((NHD.LT.0).AND.(NISOT.GT.1)) WRITE(6,616)  (SH(J),J=2,NISOT)
      WRITE(6,610) ESC
      IF((NHD.GT.0).OR.(NHD.EQ.-2)) GO TO 65
      A1=1.+1./ZN
      A2=A1-0.5
C*** GAMMA  IS THE LIBRARY GAMMA FUNCTION SUBROUTINE.  IF IT FAILS, ON
C    RETURNING TO THE CALLING PROGRAM CONTROL IS TRANSFERRED TO
C    STATEMENT 89, OTHERWISE IT GOES TO THE FOLLOWING STATEMENT.
```

```
      CALL GAMMA(A1,GM1,$62,$89)
   62 CALL GAMMA(A2,GM2,$64,$89)
   64 FCT=(ZN-2.)*SQPI/SBZ(1) *GM1/GM2
   65 CN=FCT/HN
      PW1=-1./ZN
      SY2=0.0
      JF=0
      DO 66 J=1,NISOT
      VD(J)=VH(J)/(HN*FMU(J))
      DVD(J)=0.0
      DD(J)=0.0
      JI=JF+1
      JF=JF+ISOT(J)
      DISOC=DSPR+SH(J)
      DO 66 I=JI,JF
      DY(I)=DY(I)-G(I)
      R2(I)=CN*ABS(DISOC-G(I))**PW1
   66 SY2=SY2+DY(I)**2
      DZN=0.0
      DCN=0.0
      XCN=-0.99E-31
      IF((ALOG10(CN)*ZN ).LE.33.) XCN=CN**ZN
      CN=XCN
      ERR=SQRT(SY2)
      IF(NFT.LE.NP) GO TO 70
C*** ERR  IS THE STANDARD ERROR OF THE FIT.
      ERR=ERR/SQRT(FLOAT(NFT-NP))
C*** PRINT RESULTS.
      IF(CN.LE.0.0) GO TO 70
      CALL CONFID(ERR,NFT,NP,CN,PAR,VD,DZN,DCN,DVD,DD,SCRAT)
   70 DSOC=DSPR
      DU=DSOC+DD(1)
      DL=DSOC-DD(1)
      VDU=VD(1)+DVD(1)
      VDL=VD(1)-DVD(1)
      CNU=CN+DCN
      CNL=CN-DCN
      ZNU=ZN+DZN
      ZNL=ZN-DZN
      IF(NISOT .LE.1) GO TO 74
      IF(ISH.GT.0)  WRITE(6,614)
      WRITE(6,612)  NISOT,( BZ(J),FMU(J),ISOT(J),SH(J),DD(J),VD(J),
     1   DVD(J),J=1,NISOT)
      WRITE(6,613)
   74 WRITE(6,602)  NFT,ERR,DSOC,VH(1),HN,ZN,VD(1),CN,DD(1),DZN,DVD(1),
     1  DCN,DU,ZNU,VDU,CNU,DL,ZNL,VDL,CNL
      IF(ABS(E(1)-E(2)).LT.0.01) GO TO 80
      NLIN=NFT/4+1
      WRITE(6,604)
      DO 78 J=1,NLIN
   78 WRITE(6,603)  (X(I),G(I),DY(I),R2(I),I=J,NFT,NLIN)
      GO TO 90
   80 NLIN=NFT/3+1
      WRITE(6,606)
      DO 84 J=1,NLIN
   84 WRITE(6,605)  (X(I),G(I),DY(I),R2(I),I=J,NFT,NLIN)
```

```
      GO TO 90
C*** PRINT FOR ERROR CONDITION IN GAMMA FUNCTION, SUBROUTINE GAMMA.
   89 ZN=1./(A1-1.)
      WRITE(6,607) ZN,A1,A2
   90 CONTINUE
      GO TO 4
   99 STOP
  501 FORMAT(20I4)
  502 FORMAT(8F10.3)
  503 FORMAT(16A5/10I4)
  504 FORMAT(F10.4,E10.5,6F10.3)
  505 FORMAT(5(F5.1,F10.3))
  601 FORMAT(1H1 10X,16A5/1H0 5X 59HPARAMETER UNCERTAINTIES REPRESENT A
     195/100 CONFIDENCE LIMIT  /1H0 5X  12HFIT DATA FOR I2,35H ISOTOPIC
     2SPECIES WITH  BZ VALUE(S) 5E14.7 )
  602 FORMAT(1H0/10X 20HLEAST SQUARES FIT TO,I3,22H ENERGIES HAS  STDERR
     1=    E10.4/1H0 5X 10HAND YIELDS,5X 3HE =,F10.3,4H - ( F9.4,2H -
     2  F9.6,16H*V )**(2/(1 - 2/ F7.3,4H)) , 5X 3HVD= F8.3,5X 3HCN=
     3  E11.5/ 1H0 5X 18HWITH UNCERTAINTIES F10.3,40X F7.3,12X F8.3, 8X
     4  E11.5 / 6X 12HUPPER BOUNDS 6X F10.3,40X F7.3,12X F8.3,8X E11.5/
     5            6X 12HLOWER BOUNDS 6X F10.3,40X F7.3,12X F8.3,8X E11.5 )
  603 FORMAT((4(F8.1,F10.3,2F7.3)))
  604 FORMAT(1H0/ 4(6X 1HV 7X 1HE 6X 2HDE 5X 2HR2 2X))
  605 FORMAT((3(F9.1,E13.7,E11.5,F7.3)))
  606 FORMAT(1H0/ 3(6X 1HV 9X 1HE 10X 2HDE 7X 2HR2 2X))
  607 FORMAT(1H0/10X 24HERROR.....IN GAMMA.  ZN=,E11.5,6H,  A1=,E11.5,
     1  6H,  A2=,E11.5)
  608 FORMAT(1H0 5X 17HCONSTRAIN     N = F5.2, 13H  THROUGHOUT.  )
  609 FORMAT(1H0 5X 17HCONSTRAIN     D = F10.3,13H  THROUGHOUT.  )
  610 FORMAT(1H0 5X 36HSCALE D INSIDE GASAUS BY SUBTRACTING E12.6)
  612 FORMAT(1H0 5X 7HFOR THE I2,17H ISOTOPIC SPECIES 11X 2HBZ 10X 3HFMU
     1  4X 4HISOT 5X 2HSH 13X 2HVD /(37X E13.7,F11.7,I4,2(F8.3,1H( F6.3,
     2  1H)  )))
  613 FORMAT(    6X 29HCONSTANTS BELOW FOR ISOTOPE-1)
  614 FORMAT(1H0 3X 58HCOMBINE DATA FOR DIFFERENT ISOTOPES USING KNOWN S
     1HIFTS  SH  )
  615 FORMAT(1H0 5X 18HCONSTRAIN     CN = E11.6, 13H  THROUGHOUT.  )
  616 FORMAT(17X 21HAND  ISOTOPE SHIFT(S) 4F9.4  )
      END
```

```
      SUBROUTINE CNDSRT(PAR,NP,PW,L)
C*** SUBROUTINE USED BY  MODEL  AND  GASDIF  TO SORT OUT THE POSSIBLE
C    FITTING OPTIONS. RETURNS WITH  PR1=N, PR2=KN, PR3(J)=KN*VD(J), AND
C    PR4(J)=DISOC(J)
      COMMON/BLK1/NISOT,NDSOC,X(50),FMU(4),ISOT(4),ZN,HN,VH(4),DSOC,
     1  SH(4),NHD,ESC
      DIMENSION  PAR(NP)
      L=2-NHD
      IF(NHD.GT.0) GO TO 2
      L=1
      IF(NHD.LE.-2) GO TO 2
      ZN=PAR(1)
      L=2
    2 PW=2.*ZN/(ZN-2.)
      IF(L.GT.0) HN=PAR(L)
      DO 4 J=1,NISOT
    4 VH(J)=PAR(L+J)
      IF((L+NISOT).GE.NP) GO TO 99
      K=L+NISOT
      DSOC=PAR(K+1)
      IF(NDSOC.LE.1) GO TO 99
      DO 8 J=2,NDSOC
    8 SH(J)=PAR(K+J)
   99 RETURN
      END
```

```
      SUBROUTINE MODEL(PAR,YC,NFT,NP)
C*** SUBROUTINE REQUIRED BY  GASAUS.  CALCULATES VALUES OF THE FUNCTION
C    YC(I)  AT EACH OF THE  NFT  ARRAY POINTS  X(I), FOR ANY TRIAL SET OF
C    VALUES OF THE  NP  PARAMETERS  PAR(J)
      COMMON/BLK1/NISOT,NDSOC,X(50),FMU(4),ISOT(4),ZN,HN,VH(4),DSOC,
     1  SH(4),NHD,ESC
      DIMENSION  PAR(NP),YC(NFT)
      CALL CNDSRT(PAR,NP,PW,L)
      JF=0
      DO 20 J=1,NISOT
      JI=JF+1
      JF=JF+ISOT(J)
      FHN=HN*FMU(J)
      D=DSOC+ESC+SH(J)
   18 DO 20 I=JI,JF
   20 YC(I)=D-(VH(J)-FHN*X(I))**PW
   99 RETURN
      END
```

```
      SUBROUTINE GASDIF(PAR,DYDP,NFT,NP)
C*** SUBROUTINE REQUIRED BY  GASAUS.  CALCULATES PARTIAL DERIVATIVES
C   DYDP(I,J)  OF THE FUNCTION AT EACH OF THE ARRAY POINTS  X(I) , WITH
C   RESPECT TO EACH OF THE TRIAL PARAMETER VALUES  PAR(J)
      COMMON/BLK1/NISOT,NDSOC,X(50),FMU(4),ISOT(4),ZN,HN,VH(4),DSOC,
     1  SH(4),NHD,ESC
      DIMENSION  DYDP(NFT,NP),PAR(NP),DY(50)
      CALL CNDSRT(PAR,NP,PW,L)
      PW1=PW-1.
      IF(NISOT .LE.1) GO TO 4
      JJ=L+1
      DO 2 J=JJ,NP
      DO 2 I=1,NFT
    2 DYDP(I,J)=0.0
    4 JF=0
      DO 6 J=1,NISOT
      JI=JF+1
      JF=JF+ISOT(J)
      JJ=J+L
      FHN=HN*FMU(J)
      DO 6 I=JI,JF
      DY(I)=VH(J)-FHN*X(I)
      DYDP(I,JJ)=-PW*DY(I)**PW1
      IF(L.LE.0) GO TO 6
      DYDP(I,L)=-DYDP(I,JJ)*FMU(J)*X(I)
    6 CONTINUE
      IF(NHD.EQ.-2) GO TO 99
      IF(NHD.GT.0) GO TO 10
      JF=0
      FZN=2./(ZN*(ZN-2.))
      DO 8 J=1,NISOT
      JI=JF+1
      JF=JF+ISOT(J)
      JJ=J+L
      DO 8 I=JI,JF
    8 DYDP(I,1)=-FZN*ALOG(DY(I))*DYDP(I,JJ)*DY(I)
      IF(NHD.EQ.-1) GO TO 99
   10 JF=0
      IS1=ISOT(1)
      ISOT(1)=NFT
      K=L+NISOT
      DO 14 J=1,NDSOC
      JI=JF+1
      JF=JF+ISOT(J)
      DO 12 I=JI,JF
   12 DYDP(I,K+J)=1.0
      IF(J.EQ.1) JF=IS1
   14 CONTINUE
      ISOT(1)=IS1
   99 RETURN
      END
```

```
      SUBROUTINE CONFID(ERR,NFT,NP,CN,PAR,VD,DZN,DCN,DVD,DD,DYDP)
C*** SUBROUTINE TO CALCULATE  95 PERCENT CONFIDENCE LIMITS ON THE FITTED
C    PARAMETERS. YIELDS RESULTS WHICH ARE APPROXIMATE IN ONLY ONE WAY.
C    THAT IS, IMPLICITLY ASSUME THAT THE FUNCTION IS LINEAR IN THE
C    PARAMETERS IN AN INTERVAL ABOUT THEIR BEST VALUES.
      COMMON/BLK1/NISOT,NDSOC,X(50),FMU(4),ISOT(4),ZN,HN,VH(4),DSOC,
     1  SH(4),NHD,ESC
      DOUBLE PRECISION  A(6,6),ANM(6),DT,Z
      DIMENSION PAR(NP),DVD(NISOT),DD(NISOT),T(50),VD(4),DYDP(NFT,NP),
     1  AH(6)
      DATA/T/12.706,4.303,3.182,2.776,2.571,2.447,2.365,2.306,2.262,
     1  2.228,2.201,2.179,2.160,2.145,2.131,2.120,2.110,2.101,2.093,
     2  2.086,2.080,2.074,2.069,2.064,2.060,2.056,2.052,2.048,2.045,
     3  2.042,20*2.000/
      NDIM=6
      CALL GASDIF(PAR,DYDP,NFT,NP)
      L=2
      IF(NHD.EQ.-2) L=1
      IF(NHD.GT.0) L=2-NHD
C*** MUST MODIFY THE DERIVATIVES FROM  GASDIF  SINCE THERE THE
C    INDEPENDENT VARIABLES ARE  (FMU(IS)*VD(IS)*HN), AND  HN.
      JF=0
      FDN=1./(ZN*CN)
      DO 4 IS=1,NISOT
      JI=JF+1
      JF=JF+ISOT(IS)
      JJ=L+IS
      FHN=FMU(IS)*HN
      DO 4 I=JI,JF
      DYDP(I,JJ)=FHN*DYDP(I,JJ)
      IF(L.LE.0) GO TO 4
      DYDP(I,L)=-DYDP(I,JJ)*(VD(IS)-X(I))*FDN
    4 CONTINUE
      DO 8 J=1,NP
      DO 8 K=1,J
      Z=0.0D+000
      DO 6 I=1,NFT
    6 Z=Z+DBLE(DYDP(I,J))*DBLE(DYDP(I,K))
      A(J,K)=Z
    8 A(K,J)=Z
      DO 20 J=1,NP
      ANM(J)=0.0D+000
      DO 16 K=1,NP
   16 ANM(J)=ANM(J)+DABS(A(J,K))
      DO 18 K=1,NP
   18 A(J,K)=A(J,K)/ANM(J)
   20 AH(J)=A(J,J)
      CALL DMTINV(A,NP,NDIM,DT,IER)
      DO 12 I=1,NP
      TST=AH(I)*A(I,I)
      IF(ABS(TST).GE.0.1E+07) WRITE(6,601) I,TST
      IF(A(I,I).GT.0.D+0) GO TO 12
      WRITE(6,602) I,A(I,I)
      A(I,I)=-A(I,I)
   12 A(I,I)=A(I,I)/ANM(I)
      FERR=ERR*T(NFT-NP)
```

```
      IF(L.GT.1) DZN=FERR*DSQRT(A(1,1))
      IF(NHD.LT.2) DCN=FERR*DSQRT(A(L,L))
      DO 11 J=1,NISOT
      K=L+J
   11 DVD(J)=FERR*DSQRT(A(K,K))
      IF(NHD.LT.0) GO TO 99
      DO 13 J=1,NDSOC
      K=L+NISOT+J
   13 DD(J)=FERR*DSQRT(A(K,K))
   99 RETURN
  601 FORMAT(1H0 5X ,'CAUTION *** CONFIDENCE LIMITS POSSIBLY UNRELIABLE'
     1SINCE FOR   I =' I2, '   FIND   A(I,I)*AINV(I,I) =' E10.5)
  602 FORMAT(1H0 5X 'CAUTION *** CONFIDENCE LIMITS UNRELIABLE SINCE FOR
     1 I =' I2, 5X 10HANV(I,I) = D14.7 )
      END
```

```
      SUBROUTINE DMTINV(A,N,NDIM,DET,IER)
C*** SUBROUTINE TO INVERT MATRIX  A  BY METHOD OF GAUSS-JORDAN
C    ELIMINATION WITH PARTIAL PIVOTING. INVERSE IS RETURNED IN THE
C    INPUT MATRIX  A.  ** DIMENSION OF  A  IS (NDIM*NDIM), ALTHOUGH
C    THE MATRIX TO BE INVERTED IS ONLY (N*N).   ***  IER=1  IF MATRIX
C    IS SINGULAR TO THE PRECISION OF THE MACHINE, OTHERWISE  IER=0.
C ** DET  IS THE DETERMINANT OF INPUT  A. ** EVERYTHING DOUBLE PRECISION.
C*** ROUTINE WRITTEN AND TESTED BY  R.A. LA BUDDE.
      DIMENSION A(1),ROW(100)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER ROW
      IER=0
      AU = 0.D0
      AL = 1.D+300
      DET = 1.D0
      NK = - NDIM
      DO 1000 K = 1,N
      NK = NK + NDIM
      KK = NK + K
      AMAX = A(KK)
      NI = K
      DO 200 I = K,N
      KI = NK + I
      IF (DABS(AMAX) .GE. DABS(A(KI))) GO TO 200
      AMAX = A(KI)
      NI = I
200   CONTINUE
      DET = DET*AMAX
      IF (AL .GT. DABS(AMAX)) AL = DABS(AMAX)
      IF (AU .LT. DABS(AMAX)) AU = DABS (AMAX)
```

```
      PIVRAT = AL/AU
      IF (PIVRAT .GT. 1.D-12) GO TO 300
      WRITE (6,1) K,DET,PIVRAT
      IER=1
      RETURN
  300 ROW(K) = NI
      IF (NI .EQ. K) GO TO 350
      DET = - DET
      NI = NI - NDIM
      KI = K - NDIM
      DO 250 I = 1,N
      KI = KI + NDIM
      NI = NI + NDIM
      DODA = A(KI)
      A(KI) = A(NI)
250   A(NI) = DODA
350   NI = - NDIM
      DO 800 I = 1,N
      NI = NI + NDIM
      IF (I .EQ. K) GO TO 800
      KI = NI + K
      A(KI) = A(KI)/AMAX
      DO 700 J = 1,N
      IF (J .EQ. K ) GO TO 700
      JI = NI + J
      JK = NK + J
      A(JI) = A(JI) - A(JK)*A(KI)
700   CONTINUE
800   CONTINUE
      DO 900 I = 1,N
      KI = NK + I
900   A(KI) = -A(KI)/AMAX
1000  A(KK) = 1.D0/AMAX
      NK = - NDIM
      DO 1500 K = 1,N
      NK = NK + NDIM
      IF (ROW(K) .EQ. K) GO TO 1500
      NI = (ROW(K) - 1)*NDIM
      DO 1200 J = 1,N
      JK = NK + J
      JI = NI + J
      DODA = A(JK)
      A(JK) = A(JI)
1200  A(JI) = DODA
1500  CONTINUE
      RETURN
    1 FORMAT(/'0GJR FAILS AT STEP',I6,2X,'MATRIX IS SINGULAR TO PRECISIO
     1N OF MACHINE'/5X,'DETERMINANT',D20.10/5X,'RATIO OF MIN TO MAX PIVO
     2TS',D20.10)
      END
```

```
CHLORINE B-3PI(0+U) LEVELS OF  DOUGLAS, MOLLER, AND STOICHEFF.
   1   5
 1.036912
  19  31
  876.90     873.67     868.43     860.69     849.68     834.90     815.73     791.59
  762.08     726.59     684.78     636.20     580.18     516.38     444.19     363.28
  273.25     173.48      63.68
 870.
  10   0    1    0
    5.0000 .13792+06     35.131    881.215
   8   0    1    0
    5.0000 .12520+06     34.900    880.248
   6   0    1    0
    5.0000 .11863+06     34.800    879.886
   5   0    1    0
    5.0000 .11923+06     34.814    879.865
   4   0    1    0
    5.0000 .12586+06     34.907    879.964
BROMINE B-3PI(0+U) LEVELS OF HORSLEY AND BARROW FOR (79,79) AND (81,81) ISOTOPES
   2   4
 2.34018    2.39944
   4  53
  574.47     571.77     568.20     563.65
   4  53
  574.81     571.61     567.45     562.28
 570.
   8   0    0    0
    6.0843 .31322+07     59.067     59.811    579.157      2.029
   8   0    0    1
    6.0843 .31322+07     59.067     59.811    579.157      2.029
   8   0    1    0
    5.0000 .17666+06     60.479     61.240    579.685      2.029
   8   0    1    1
    5.0000 .17666+06     60.479     61.240    579.685      2.029
```