ROTATIONAL CONSTANTS OF H_2Se AND D_2Se FROM THEIR INFRARED SPECTRA

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John Tressler

AN ABSTRACT OF A THESIS

Submitted to
the College of Science and Arts,
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Department of Physics and Astronomy

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ABSTRACT

An analysis of the infrared spectra of H_2Se and D_2Se is made in order to determine the rotational constants and the first order stretching coefficients of these molecules. The analysis utilizes the energy moment treatment of the quantum mechanical asymmetric rotator developed by Parker and Brown.

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Table of contents

List of tables

List of figures

I

Introduction

In order to discuss the rotational energies of nonlinear polyatomic molecules, it is both customary and convenient to classify them according to the relative magnitudes of their principal moments of inertia. The principal moments of inertia are expressed in terms of a body-fixed coordinate system which has its origin at the center of mass of the molecule and is so oriented that the product of inertia terms are all zero. Depending upon the geometry of the molecule, the three moments of inertia may all have the same value, or two may have the same value but differ from the third, or all three may have different values. The molecules are then classified as spherical tops, symmetrical tops, and asymmetrical tops respectively.

The vibration-rotation energies of asymmetrical tops can be formulated in terms of a quantum mechanical Hamiltonian function.[1] To a first approximation the vibrational energy of the molecule is that of an ensemble of harmonic oscillators, and the rotational part of the energy is that of a semi-rigid microphysical rotator.

The total energy expressed by the Hamiltonian can then in this approximation be set down as the sum of two terms, a

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[1] H.H. Nielsen, Rev. Mod. Physics <u>23,</u> 90 (1951)

vibrational and a rotational term. If the forces of attraction between the atoms of a molecule are considered strong enough to hold the molecule almost rigid, it is found to a good approximation that the rotational energy can be separated from the vibrational energy. Thus, if one considers transitions for which the electronic configuration remains unchanged and for which the vibrational energy remains unchanged, then the case dealt with is one of "pure rotation", and the rotational energies are added to the energy of vibration of the molecule vibrating in one of its normal modes. When this approximation is inadequate, a second-order correction term involving both rotation and vibration is necessary to account for the change in the average moment of inertia due to vibration-rotation interaction, and depending on the molecule and energy levels considered a correction term may be needed to adjust for the change in the moment of inertia caused by centrifugal stretching of the molecule.

In their literature, Parker and Brown[2, 3, 4] describe a procedure which relates the energies of a stationary quantum mechanical system to the physical constants appearing in the Hamiltonian describing this system.

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[2] P. M. Parker and L. C. Brown, Amer. J. Phys. 27, 509 (1959)
[3] P. M. Parker and L. C. Brown, J. Chem. Phys. 27, 1108, (1957)
[4] P. M. Parker and L. C. Brown, J. Chem. Phys. 30, 909 (1959)

Utilization of this method makes it possible to compute the effective rotational constants of a molecule from spectroscopic data. The method described by Parker and Brown deals not only with the rigid rotator,[3, 4] but is extended to include first order centrifugal stretching effects.[5]

The present work utilizes this energy moment treatment of the quantum mechanical asymmetrical rotator developed by Parker and Brown[3, 4, 5] for the analysis of the infrared spectral data of D_2Se and H_2Se obtained by Palik and Oetjen.[6, 7] The effective rotational constants of D_2Se and H_2Se are calculated for the rigid case; the stretching coefficients as well as the rotational constants are determined for the non-rigid case.

An error analysis is made and the results are compared with the rotational constants which Palik and Oetjen[6, 7] obtained by applying a different method of analysis to the same data.

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[3] P. M. Parker and L. C. Brown, J. Chem. Phys. 27, 1108, (1957)

[4] P. M. Parker and L. C. Brown, J. Chem. Phys. 30, 909 (1959)

[5] P. M. Parker and L. C. Brown, J. Chem. Phys. 31, 1227, (1959)

[6] E. D. Palik and R. A. Oetjen, J. Molecular Spectroscopy, 1, 223, (1959)

[7] E. D. Palik and R. A. Oetjen, J. Molecular Spectroscopy, 3, 259, (1959)

II

Theory

(a) Rigid rotator analysis

The energies of a rigid quantum mechanical system can be expressed by a Schroedinger equation,

$$W\phi_k = F_k \phi_k \qquad (2a.1)$$

where W is the appropriate Hamiltonian for the system, k enumerates the members of a supposedly complete set of energy eigenfunctions ϕ, and F_k their corresponding eigenvalues.

When it is possible to express the matrix elements W_{ij} of the Hamiltonian W in some convenient representation ψ_k, the allowed energies of the system F_k are the roots of the secular equation,

$$\left| W_{ij} - F\delta_{ij} \right| = 0, \qquad (2a.2)$$

where   is the Kronecker delta symbol. This secular equation can be expanded into a polynomial of degree n in the form,

$$F^1 + c_1 F^{n-1} + c_2 F^{n-2} + \ldots\ldots + c_n = 0, \qquad (2a.3)$$

in which the n roots of F and the n coefficients form a complete set of invariants of the matrix. The subsequent determination of the physical constants of the system can in certain cases be effected by equating values of c_i expressed in terms of experimentally determined energy levels to the corresponding values of c_i expressed in terms of the matrix elements W which contain the physical

parameters. Parker and Brown[3] show that these constants c_i can be expressed in terms of the first r moments of the energy levels.

$$S_r = \sum_{\tau} (F_{\tau})^r \qquad (2a.4)$$
$$\tau = 1, 2, 3, \ldots, n ,$$

and alternately by the equation,

$$S_i = \mathrm{Tr}(W^i) \qquad (2a.5)$$
$$i = 1, 2, 3, \ldots, n ,$$

where S_r represents the moments of the energy levels, and $\mathrm{Tr}(W^i)$ are the traces of the submatrices of the Schroedinger equation; their method is then developed in terms of moments of the energy levels rather than in terms of the polynomial coefficients.

In applying this method to the rigid asymmetric rotator problem, the Hamiltonian for the system is

$$W = H/hc = AP_x{}^2 + BP_y{}^2 + CP_z{}^2 . \qquad (2a.6)$$

Here P_x, P_y, and P_z are components of angular momentum of the rotator in units of $\hbar$ referred to the body-fixed coordinate system which is defined by the diagonal inertia tensor; and

$$A = h/8\pi^2 I_x c, \;\; B = h/8\pi^2 I_y c, \;\; C = h/8\pi^2 I_z c . \qquad (2a.7)$$

The constants A, B, and C are the reciprocals of the effective principal moments of inertia I_x, I_y, and I_z apart from universal

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[3] P. M. Parker and L. C. Brown, J. Chem. Phys. 27, 1108, (1957)

constants.

It is shown[2] that the first three moments are adequate in the determination of A, B, and C. The value of the first moment S_1 is obtained from the experimental data by adding the (2J + 1) levels F corresponding to a fixed value of J; the electronic state is assumed to remain fixed throughout the procedure. The first moments is given by the equation

$$S_1 = \Sigma\ (F_\tau) \tag{2a.8}$$

$$\tau = J,\ J-1,\ \ldots,\ -J\ .$$

The mean value of the energies $\overline{F}_J$ corresponding to a given J is next found by dividing S_1 by the number of terms in the summation:

$$\overline{F}_J = S_1/2J+1. \tag{2a.9}$$

Subtraction of $\overline{F}_J$ from each of the (2J+1) values of F_τ yields

$$F^o_\tau = (F_\tau - \overline{F}_J). \tag{2a.10}$$

This modifying process shifts the zero level equally for all energies considered, but does not change any of the physical aspects of the problem. The second and third moments can then be evaluated by squaring and cubing the sum of the (2J+1) modified energies,

$$S_2 = \Sigma\ (F^o_\tau)^2 \tag{2a.11}$$

$$S_3 = \Sigma\ (F^o_\tau)^3 \tag{2a.12}$$

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[2] P. M. Parker and L. C. Brown, Amer. J. Phys. 27, 509 (1959)

It can then be shown that[3, 4]

$$S_1 = p_1 \alpha \tag{2a.13}$$

$$S_2 = p_2 \gamma^2 (1+\beta^2/3) \tag{2a.14}$$

$$S_3 = p_3 \gamma^3 (1-\beta^2) \tag{2a.15}$$

The quantities p_1, p_2, and p_3 are polynomials in J as follows:

$$p_1 = 2J(J+1)(2J+1)/3! \tag{2a.16}$$

$$p_2 = 2J(J+1)(2J-1)(2J+1)(2J+3)/3(5!) \tag{2a.17}$$

$$p_3 = 2J(J+1)(2J-3)(2J-1)(2J+1)(2J+3)(2J+5)/3(7!) \tag{2a.18}$$

The parameter α, which is a measure of an equivalent spherical rotator, now follows from (2a.13). The parameter β measures the deviation from a symmetrical top, and has a value that lies in the range $-1 \leqslant \beta \leqslant 0$. Its value can be determined by employing (2a.14) and (2a.15) simultaneously to give

$$1 - \delta = (1-\beta^2)^2/(1+\beta^2/3)^3 = p_2{}^3 S_3{}^2/p_3{}^2 S_2{}^3 , \tag{2a.19}$$

where δ is first determined from the experimental data and β is then obtainable from a tabulation of β in terms of δ. Having determined β, then γ, which shows the deviation of the top from spherical symmetry, is given by (2a.14).

When α, β, and γ are known, A, B, and C can be found by solving the equations

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[3] P. M. Parker and L. C. Brown, J. Chem. Phys. 27, 1108, (1957)

[4] P. M. Parker and L. C. Brown, J. Chem. Phys. 30, 909 (1959)

$$A = (1/3)[\alpha - \gamma/2(1-\beta)] \qquad (2a.20)$$

$$B = (1/3)[\alpha - \gamma/2(1+\beta)] \qquad (2a.21)$$

$$C = (1/3)[\alpha + \gamma] \ . \qquad (2a.22)$$

The principal moments of inertia readily follow from equations (2a.7).

(b) Non-rigid rotator analysis

The basic scheme of vibration-rotation energies is expressed by the harmonic oscillator and rigid rotator formulas. However, a precise quantitative adjustment to spectral data must consider both the anharmonicity of the potential energy and the centrifugal stretching of the rotating molecule. Only the effects of stretching are considered here.

To correct for non-rigidity, one may set down a Hamiltonian of the form

$$W = W_o + W_1, \qquad (2b.1)$$

$$W_o = AP_x^2 + BP_y^2 + CP_z^2 \qquad (2b.2)$$

is the Hamiltonian of the rigid rotator, and W_1 is the centrifugal distortion term which can be written to a first order in the following form[5]:

$$W_1 = \sigma_1 P_x^4 + \sigma_2 P_y^4 + \sigma_3 P_z^4 + \sigma_4(P_y^2P_z^2 + P_z^2P_y^2) + \sigma_5(P_x^2P_z^2 + P_z^2P_x^2) + \sigma_6(P_x^2P_y^2 + P_y^2P_x^2) \ . \qquad (2b.3)$$

The coefficients σ depend on the geometrical form and the

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[5] P. M. Parker and L. C. Brown, J. Chem. Phys. 31, 1227, (1959)

force constants of the molecule and their values can in principle be determined from experimental data. The moment equations of (2b.1) are then shown to be[5]:

$$S_1/p_1\gamma = (\alpha/\gamma)[+(3/2)[\alpha_1(3f-1)+\alpha_2(2f+1)]]; \qquad (2b.4)$$

$$S_2/p_2\gamma^2 = (1+\beta^2/3)+2(6f-5)\gamma_1(1+\beta\beta_1)- 4(f+5)\gamma_2(1+\beta\beta_2); \qquad (2b.5)$$

$$S_3/p_3\gamma^3 = (1-\beta^2)+9(f-2)(1+\beta^2/3)(\alpha_1-\alpha_2)+ 21\gamma_1(f-1)[(1-\beta^2/3)-2\beta\beta_1]- 42\gamma_2[(1-\beta^2/3)-2\beta\beta_2]. \qquad (2b.6)$$

In these moment equations,

$$\sigma_i = (15/2)\gamma\lambda_i \qquad i = 1, 2, \ldots, 6, \qquad (2b.7)$$

$$\alpha_1 = (\lambda_1+\lambda_2+\lambda_3), \qquad (2b.8)$$

$$\alpha_2 = (\lambda_4+\lambda_5+\lambda_6), \qquad (2b.9)$$

$$\beta_1 = (\lambda_1-\lambda_2)/(2\lambda_3-\lambda_1-\lambda_2), \qquad (2b.10)$$

$$\beta_2 = (\lambda_4-\lambda_5)/(2\lambda_6-\lambda_4-\lambda_5), \qquad (2b.11)$$

$$\gamma_1 = (15/14)(2\lambda_3-\lambda_1-\lambda_2), \qquad (2b.12)$$

$$\gamma_2 = (15/14)(2\lambda_6-\lambda_4-\lambda_5), \qquad (2b.13)$$

$$f = J(J+1) \qquad (2b.14)$$

Application of the three moment equations to three different values of J yields a set of nine equations which can be solved in principle for the nine physical parameters α, β, γ, α_1, β_1, γ_1, α_2, β_2, γ_2. The stretching constants λ_i can then

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[5] P. M. Parker and L. C. Brown, J. Chem Phys. 31, 1227, (1959)

be calculated by means of equations (2b.8) through (2b.13). The constants σ_i then follow from (2b.7).

(c) Non-rigid rotator analysis with "initial conditions"

The procedure of calculating the values of the nine physical parameters is simplified a great deal if α, β, and γ are found by extrapolation to J = 0 as in a rigid rotator analysis by employing the following method.

Equation (2b.4) can be arranged in the form

$$S_1/p_1 = \alpha + (3/2)\gamma\,(\alpha_2 - \alpha_1) + (3/2)\gamma\left[3\alpha_1 + 2\alpha_2\right] f. \tag{2c.1}$$

It is seen on a graph of S_1/p_1 vs. f that (2c.1) is the equation of a straight line with intercept

$$\alpha + (3/2)\gamma(\alpha_2 - \alpha_1) \tag{2c.2}$$

and with slope

$$(3/2)\gamma(3\alpha_1 + 2\alpha_2). \tag{2c.3}$$

Then if the "initial condition" is imposed that for J = 0

$$S_1/p_1 = \alpha\ , \tag{2c.4}$$

it must follow that

$$(3/2)(\alpha_2 - \alpha_1) = 0, \qquad \alpha_1 = \alpha_2 \tag{2c.5}$$

In imposing the "initial conditions" it is assumed that the α extrapolated to J = 0 obtained by the rigid analysis is the "unstretched" or "true" value of α. Using the values of α_1 and α_2 resulting from these conditions, the slope $(S1)_1$ of the line in equation (2c.1) is

$$(S1)_1 = (15/2)\gamma\alpha_1 . \qquad (2c.6)$$

Next, equation (2b.5) can be arranged in the following form:

$$\begin{aligned} S_2/p_2 = {} & \left[(1+\beta^2/3) - 10\gamma_1 - 10\beta\beta_1\gamma_1 - 20\gamma_2 - 20\beta\beta_2\gamma_2\right]\gamma^2 \\ & + \left[12\gamma_1 + 12\beta\beta_1\gamma_1 - 4\gamma_2 - 4\beta\beta_1\gamma_2\right]\gamma^2 f, \qquad (2c.7) \end{aligned}$$

again the equation of a straight line with the first bracketed term equal to the intercept and the second bracketed term equal to the slope of the line. Extrapolating to J = 0, it becomes

$$S_2/p_2 = \gamma^2\left[(1+\beta^2/3) - 10\gamma_1 - 10\beta\beta_1\gamma_1 - 20\beta\beta_1\gamma_2\right] . \qquad (2c.8)$$

Imposing the condition that at J = 0,

$$S_2/p_2 = \gamma^2(1 + \beta^2/3) \qquad (2c.9)$$

requires that

$$\gamma_1(1+\beta\beta_1) + 2\gamma_2(1+\beta\beta_2) = 0 , \qquad (2c.10)$$

and slope $(S1)_2$ then becomes

$$(S1)_2 = -28\gamma^2\gamma_2(1+\beta\beta_2) . \qquad (2c.11)$$

Now, since $\alpha_1 = \alpha_2$, the third moments equation arranged in slope-intercept form becomes

$$\begin{aligned} S_3/p_3\gamma^3 = {} & (1-\beta^2) - 21\gamma_1\left[(1-\beta^2/3) - 2\beta\beta_1\right] \\ & - 42\gamma_2\left[(1-\beta^2/3) - 2\beta\beta_2\right] + 21\gamma_1\left[1-\beta^2/3 - 2\beta\beta_1\right] f . \end{aligned}$$

$$(2c.12)$$

This time the condition imposed at J = 0 is

$$S_3/p_3 = \gamma^3(1-\beta^2) , \qquad (2c.13)$$

requiring that

$$\gamma_1 \left[(1-\beta^2/3 - 2\beta\beta_1)\right] - 2\gamma_2 \left[(1-\beta^2/3 - 2\beta\beta_2)\right] = 0. \qquad (2c.14)$$

The slope $(S1)_3$ is then

$$(S1)_3 = 21\gamma^3\gamma_1(1-\beta^2/3 - 2\beta\beta_1). \qquad (2c.15)$$

If the value of γ_1 is found from equation (2c.10) and then substituted in (2c.14), the following equation results after some algebraic manipulation:

$$(\beta_2 - \beta_1)(\beta^2/3 - 3) = 0. \qquad (2c.16)$$

As $\beta \neq 0$, it follows that $\beta_1 = \beta_2$; and if this fact is used in conjunction with equation (2c.10) it is found also that $\gamma_1 = -2\gamma_2$. Solving equation (2c.11) for γ_2 yields

$$\gamma_2 = -(S1)_2/\ 28\gamma^2(1+\beta\beta_2). \qquad (2c.17)$$

Here it is seen that γ_2 is expressed, with the exception of β_2, in terms of parameters that can be determined by a rigid analysis. The value of β_2 can be found, however, in terms of similar parameters by solving (2c.11) and (2c.15) simultaneously, and by using the additional information that $\beta_1 = \beta_2$ and $\gamma_2 = -\gamma_1/2$.

The resulting expression for β_2 is

$$\beta_2 = \frac{3\gamma(S1)_2(1-\beta^2/3) - 2(S1)_3}{2\beta\left[(S1)_3 + 3\gamma(S1)_2\right]}. \qquad (2c.18)$$

Substitution of α_1, β_1, and γ_1 in terms of α_2, β_2, and γ_2 respectively in equations (2.b8) through (2b.13) leads to the equations for the stretching constants λ_i:

$$\lambda_1 = 1/3\left[\alpha_1 -(7/15)\gamma_1(1-3\beta_1)\right], \qquad (2c.19)$$

$$\lambda_2 = 1/3\left[\alpha_1 -(7/15)\gamma_1(1+3\beta_1)\right], \qquad (2c.20)$$

$$\lambda_3 = 1/3\left[\alpha_1 +(14/15)\gamma_1\right], \qquad (2c.21)$$

$$\lambda_4 = 1/3\left[\alpha_2 -(7/15)\gamma_2(1-3\beta_2)\right], \qquad (2c.22)$$

$$\lambda_5 = 1/3\left[\alpha_2 -(7/15)\gamma_2(1+3\beta_2)\right], \qquad (2c.23)$$

$$\lambda_6 = 1/3\left[\alpha_2 +(14/15)\gamma_2\right]. \qquad (2c.24)$$

If it is possible to obtain α, β, and γ along with $(S1)_1$, $(S1)_2$, and $(S1)_3$ from an analysis of experimental data, α_1 can then be found by (2c.6), γ_2 by (2c.17) and β_2 by (2c.18). All stretching constants, λ_i, follow from equations (2c.19) through (2c.24). Knowledge of these values then makes it possible to determine the coefficients σ_i, of the centrifugal stretching correction terms by employing equation (2b.7).

(d) Intercept-slope method of analysis

If the rotating molecule were strictly a rigid rotator, the effective values of α, β, and γ would be constants unaffected by changes in angular momentum as shown by the equations:

$$S_1/p_1 = \alpha, \qquad (2d.1)$$

$$S_2/p_2 = \gamma^2(1+\beta^2/3), \qquad (2d.2)$$

$$S_3/p_3 = \gamma^3(1-\beta^2). \qquad (2d.3)$$

Graphs of S_i/p_i vs. $J(J+1)$ are straight lines with zero slope showing that the constants are unaffected by a change in the angular momentum quantum number J.

Analysis of experimental data shows that stretching due to centrifugal force does occur, resulting in changes in these parameters. One may, however, attempt to find the value of S_i/p_i for J = 0 by fitting the effective values of S_i/p_i obtained from an analysis of experimental data to curves of the form

$$S_i/p_1 = \alpha + \mu_1, \tag{2d.4}$$

$$S_2/p_2 = \gamma^2(1 + \beta^2/3) + \mu_2 f, \tag{2d.5}$$

$$S_3/p_3 = \gamma^3(1 - \beta^2) + \mu_3 f, \tag{2d.6}$$

where a straight line fit is obtained by applying the method of least squares.[8] The μ_i represent the slopes of the curves and are to be interpreted as a measure of the deviation from the zero-order rigid rotator theory; and in order for this first order correction to be adequate for a given system, the slopes must be very small.

Where this correction is adequate, extrapolation of the S_i/p_i curves to J = 0 enables one to determine the "true" values of the principal moments of inertia.

The first order theory is approximate even for small values of J; even for moleculesthat are not very "stretchy" the approximation becomes progressively poorer at higher values of J and higher order correction terms become necessary. In

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[8] See for example C. G. Lambe, Elements of Statistics, Chapter VII, (Longmans Green and Co., New York, 1952)

this case, the S_i/p_i vs. f curves would no longer be straight lines.[5]

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[5] P. M. Parker and L. C. Brown, J. Chem Phys. <u>31</u>, 1227, (1959)

III

Analysis

Symmetric, nonlinear, triatomic molecules like H_2Se and D_2Se have three fundamental vibration-rotation bands, ν_1, ν_2, and ν_3. Associated with the fundamental modes of vibration are the quantum numbers V_1, V_2, and V_3; which serve to describe the vibrational energy state. In the following procedure, analyses of the rotational levels associated with a fixed mode of vibration are carried out.

The geometry for both D_2Se and H_2Se is shown in Fig. 1, where it is seen that the principal axes are so oriented that the Z axis is normal to the plane of the molecule. Both molecules are asymmetric rotators with principal moments of inertia $I_z > I_y > I_x$; and rotational constants $A > B > C$.

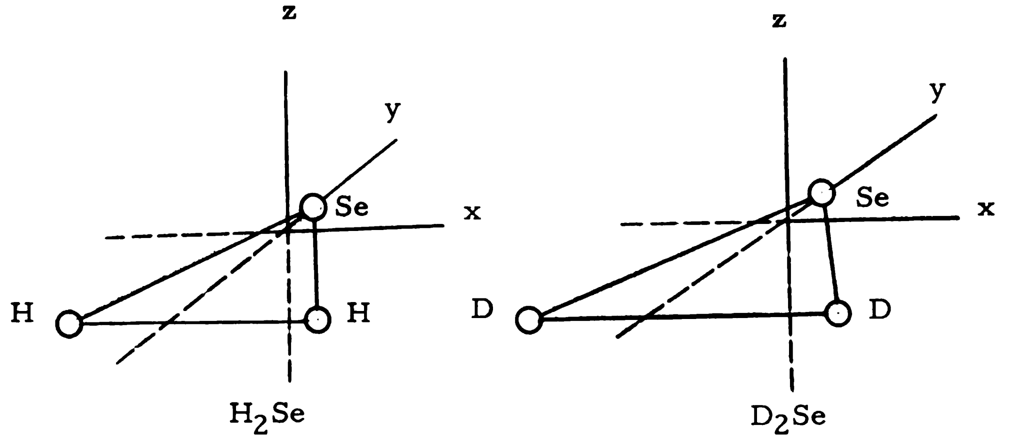

Figure 1. Geometry of the H_2Se and D_2Se molecules.

The data used in the analysis were taken from the works of Palik and Oetjen[6, 7] as follows:

H_2Se for the vibrational state $V_1 = V_2 = V_3 = 0$;

J = 0 to J = 7 from the first paper[6],

J = 8 to J = 10 from the second paper[7].

H_2Se for the vibrational state $V_1 = V_3 = 0$, $V_2 = 1$;

J = 1 to J = 6 from the second paper[7].

D_2Se for the vibrational state $V_1 = V_2 = V_3 = 0$;

J = 0 to J = 6 from the second paper[7].

D_2Se for the vibrational state $V_1 = V_3 = 0$, $V_2 = 1$;

J = 1 to J = 3 from the second paper[7].

Following the procedure discussed in part II (a), and employing equations (2a.8) through (2a.21) a rigid analysis of the preceding data was carried out. Five significant figures were retained in all calculations and the physical parameters resulting from the analysis are listed in Table I, Table II, Table III, and Table IV. These are the effective values of the parameters.

Next, the values of S_i/p_i corresponding to a given value of J were determined from the data given in Tables I through IV. The S_i/p_i along with the J(J+1) for a given J are tabulated in Tables V through VIII. Preliminary plots of S_i/p_i vs.

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[6] E.D. Palik and R.A. Oetjen, J. Molecular Spectroscopy, 1, 223, (1959)

[7] E.D. Palik and R.A. Oetjen, J. Molecular Spectroscopy, 3, 259, (1959)

Table I - Calculated physical parameters of the H_2Se molecule for the vibrational state $V_1 = V_2 = V_3 = 0$ *

J	α	$-\beta$	γ	A	B	C	S_1	S_2	$-S_3$
1	19.785	.17135	8.0399	8.1647	7.7053	3.9150	39.570	10.879	-14.012
2	19.786	.17793	8.0305	8.1720	7.6956	3.9187	197.86	22.810	367.12
3	19.782	.17410	8.0290	8.1650	7.6993	3.9177	553.89	1367.4	8281.2
4	19.773	.16830	8.0250	8.1537	7.7033	3.9160	1186.4	5005.5	59,893
5	19.764	.16166	8.0169	8.1403	7.7080	3.9157	2174.0	13,906	2.6908×10^5
6	19.750	.15559	8.0003	8.1240	7.7093	3.9167	3594.5	32,294	9.1106×10^5
7	19.735	.15161	7.9840	8.1107	7.7073	3.9170	5525.8	66,247	2.5520×10^6
8	19.719	.14665	7.9670	8.0953	7.7060	3.9173	8045.4	123900	6.2335×10^6
9	19.700	.13880	7.9444	8.0780	7.7070	3.9187	11,229	215419	1.3700×10^7
10	19.678	.13090	7.9226	8.0530	7.7073	3.9187	15,153	354010	2.7734×10^7

* α, γ, A, B, and C in units of cm^{-1}; S_1 in units of cm^{-1}, S_2 in units of cm^{-2}, S_3 in units of cm^{-3}; β is dimensionless.

Table II - Calculated physical parameters of the H_2Se molecule for the vibrational state $V_1 = V_3 = 0$; $V_2 = 1$ *

J	α	$-\beta$	γ	A	B	C	S_1	S_2	$-S_3$
1	19.670	.16054	9.5300	8.5843	7.8900	3.3800	39.340	15.267	-23.423
2	20.167	.17995	8.5656	8.4070	7.8930	3.8670	201.67	259.57	456.08
3	20.159	.17714	8.5467	8.3963	7.8917	3.8707	564.44	1550.0	9977.8
4	20.150	.18579	8.5455	8.4057	7.8763	3.8680	1209.0	5687.6	71,798
5	20.139	.16592	8.5192	8.3683	7.8973	3.8733	2215.3	15,717	323530

* α, γ, A, B, and C in units of cm^{-1}; S_1 in units of cm^{-1}, S_2 in units of cm^{-2}, and S_3 in units of cm^{-3}; β is dimensionless.

Table III - Calculated physical parameters of the D_2Se molecule for the vibrational state $V_1 = V_2 = V_3 = 0$ *

J	α	$-\beta$	γ	A	B	C	S_1	S_2	$-S_3$
1	10.045	.24266	4.0899	4.1953	3.8647	1.9850	20.090	2.8425	-1.7888
2	10.048	.23801	4.0868	4.1927	3.8683	1.9871	100.48	59.563	48,296
3	10.048	.23854	4.0863	4.1927	3.8680	1.9872	281.33	357.31	1061.8
4	10.047	.23930	4.0866	4.1930	3.8670	1.9868	602.83	1310.5	7667.5
5	10.048	.23910	4.0867	4.1933	3.8677	1.9871	1105.2	3650.5	34,504
6	10.048	.24087	4.0852	4.1943	3.8633	1.9876	1828.7	8513.9	117090

*α, γ, A, B, and C in units of cm^{-1}; S_1 in units of cm^{-1}, S_2 in units of cm^{-2}, S_3 in units of cm^{-3}; β is dimensionless.

Table IV - Calculated physical parameters of the D_2Se molecule for

the vibrational state $V_1 = V_3 = 0$; $V_2 = 1$ *

J	α	$-\beta$	γ	A	B	C	S_1	S_2	$-S_3$
1	10.135	.26770	4.1498	4.3120	3.9177	1.9051	20.270	2.9389	-1.8430
2	10.182	.22376	4.2725	4.2653	3.9467	1.9698	101.82	64.956	55.562
3	10.184	.28551	4.2623	4.3080	3.9023	1.9739	285.15	391.88	1173.5

*α, γ, A, B, and C in units of cm^{-1}; S_1 in units of cm^{-1}, S_2 in units of cm^{-2}, S_3 in units of cm^{-3}; β is dimensionless.

Table V - S_i/p_i for the H_2Se molecule in the vibrational state *

$V_1 = V_2 = V_3 = 0$

J	S_1/p_1	S_2/p_2	$-S_3/p_3$
1	19.785	65.274	504.43
2	19.786	65.171	501.50
3	19.782	65.114	501.89
4	19.773	65.006	502.15
5	19.764	64.830	501.77
6	19.750	64.523	499.68
7	19.735	64.234	497.26
8	19.719	63.932	494.84
9	19.700	63.518	491.76
10	19.678	63.125	488.70

Table VI - S_i/p_i for the H_2Se molecule in the vibrational state *

$V_1 = V_3 = 0; V_2 - 1$

J	S_1/p_1	S_2/p_2	$-S_3/p_3$
1	19.670	91.602	843.23
2	20.167	74.163	608.11
3	20.159	73.810	604.73
4	20.150	73.865	602.52
5	20.139	72.273	603.26

* S_1/p_1 in units of cm^{-1}, S_2/p_2 in units of cm^{-2}, S_3/p_3 in units of cm^{-3}.

Table VII - S_i/p_i for the D_2Se molecule in the vibrational state *

$V_1 = V_2 = V_3 = 0$

J	S_1/p_1	S_2/p_2	$-S_3/p_3$
1	10.045	17.055	64.397
2	10.048	17.018	64.395
3	10.048	17.015	64.352
4	10.048	17.019	64.343
5	10.048	17.019	64.345
6	10.048	17.011	64.220

Table VIII - S_i/p_i for the D_2Se molecule in the vibrational state *

$V_1 = V_3 = 0; V_2 = 1$

J	S_1/p_1	S_2/p_2	$-S_3/p_3$
1	10.135	17.633	66.388
2	10.182	18.559	74.083
3	10.184	18.661	71.121

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* S_1/p_1 in units of cm^{-1}, S_2/p_2 in units of cm^{-2}, S_3/p_3 in units of cm^{-3}.

(J+1) indicated that the data for the vibrational state described by the quantum numbers $V_1 = V_3 = 0$, $V_2 = 1$ for both D_2Se and H_2Se were not only too limited, but also very erratic, no further analysis was attempted.

Further analysis of the data corresponding to the vibrational ground state ($V_1 = V_2 = V_3 = 0$) was carried out for both molecules, but here too, some values were discarded. Only the values below the solid lines in the columns in Tables V and VII were used in the subsequent analysis.

The method of least squares was then applied to the data in Table V and Table VII in order to obtain the straight line best fitted to these data. The six equations which resulted are:

H_2Se ($V_1 = V_2 = V_3 = 0$)

$$S_1/p_1 = [19.795 - .0010595\ J(J+1)]\ \text{cm}^{-1} \tag{3.1}$$

$$S_2/p_2 = [65.431 - .021057\ J(J+1)]\ \text{cm}^{-2} \tag{3.2}$$

$$S_3/p_3 = [-506.55 + .16322\ J(J+1)]\ \text{cm}^{-3} \tag{3.3}$$

D_2Se ($V_1 = V_2 = V_3 = 0$)

$$S_1/p_1 = [10.048]\ \text{cm}^{-1} \tag{3.4}$$

$$S_2/p_2 = [17.019 - .00012621\ J(J+1)]\ \text{cm}^{-2} \tag{3.5}$$

$$S_3/p_3 = [-64.421 + .004085\ J(J+1)]\ \text{cm}^{-3} \tag{3.6}$$

Graphs of these equations are shown in Figs. 2, 3, 4, 5, 6, and 7.

Extrapolation of these curves yielded the values of S_i/p_i corresponding to J = 0. A rigid analysis of these extrapolated values gave the rotational constants of the molecules which are listed in Table IX.

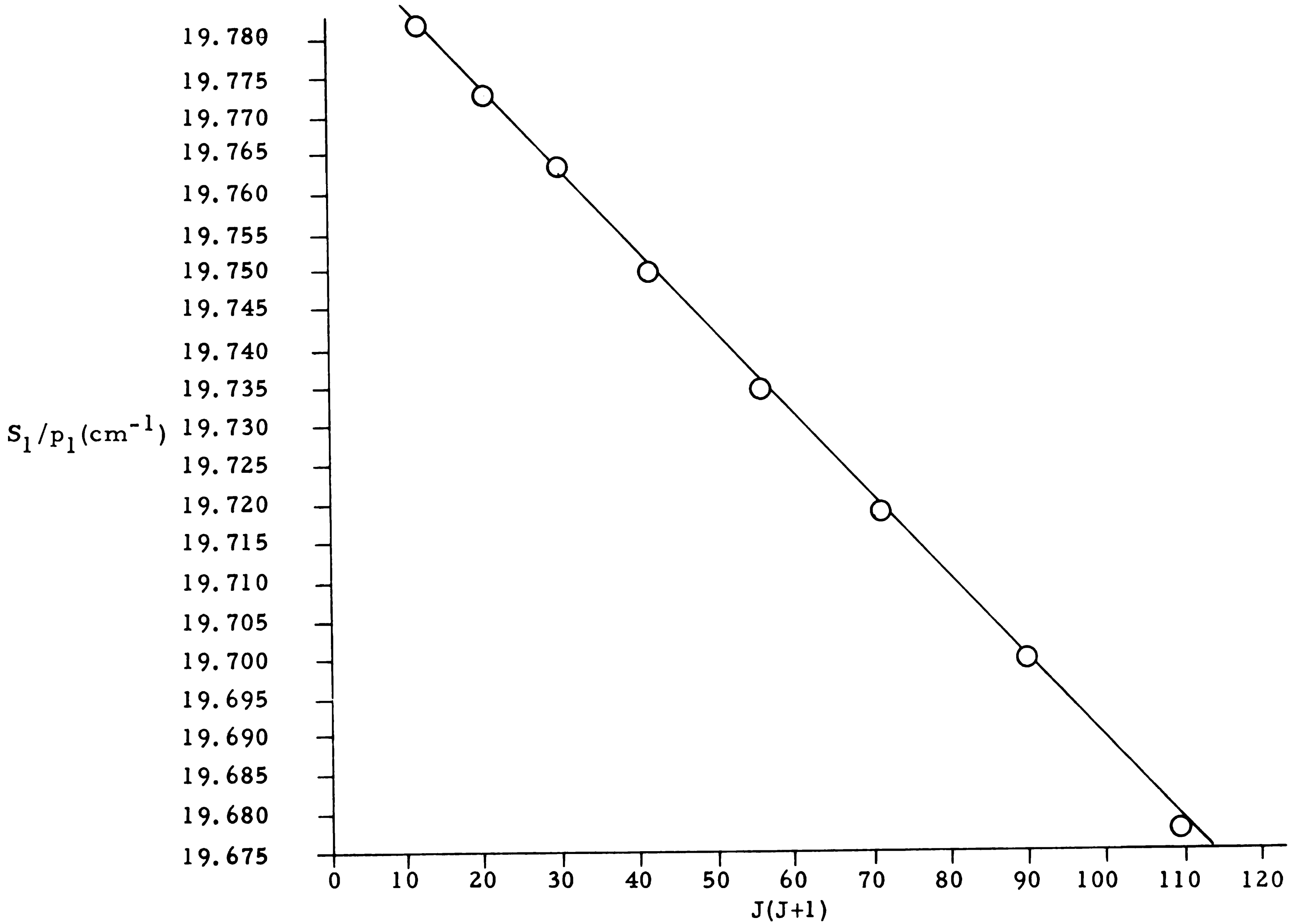

Figure 2. Plot of S_i/p_i vs.J(J+1) for the H_2Se molecule ($V_1 = V_2 = V_3 = 0$)

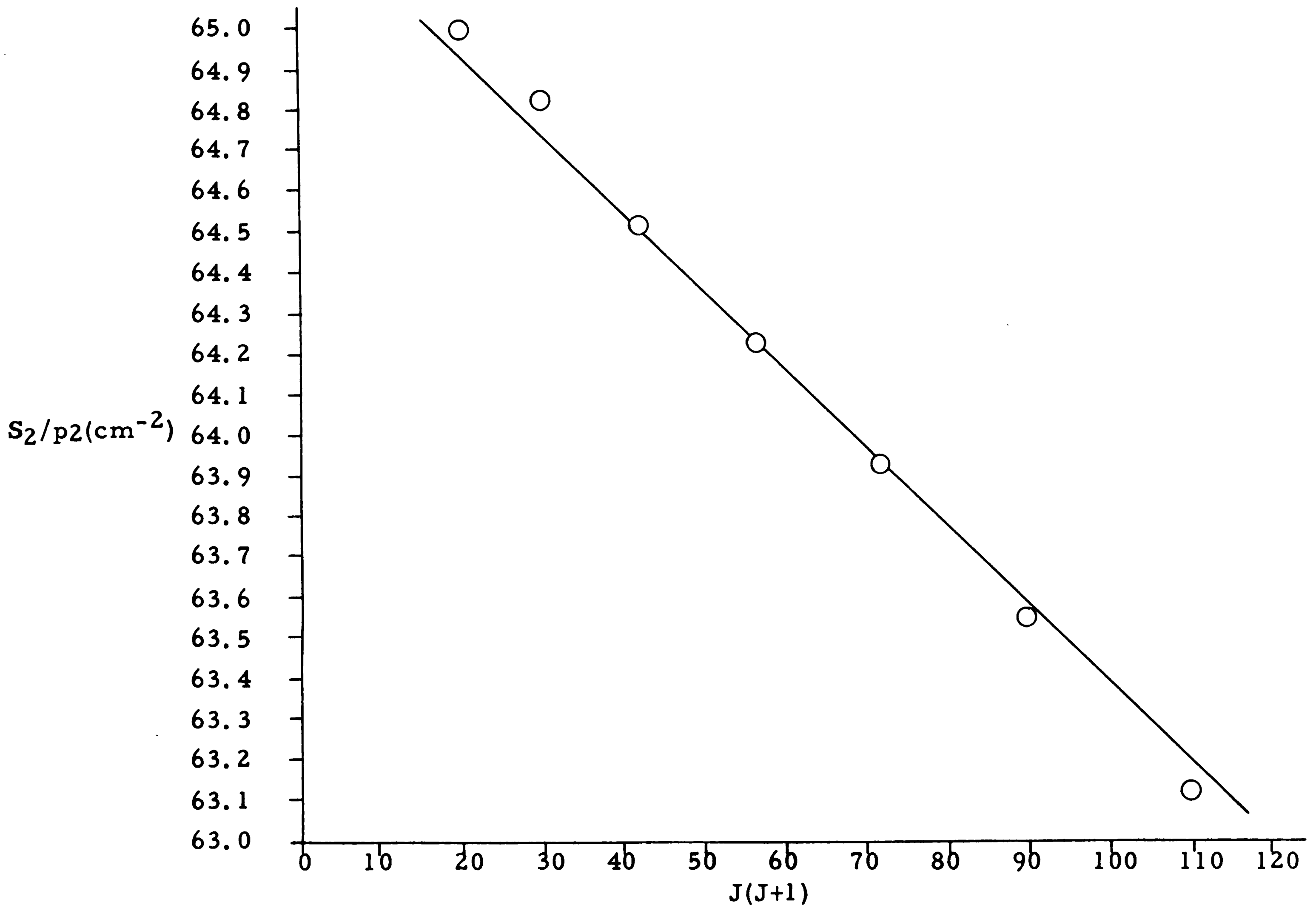

Figure 3. Plot of S_2/p_2 vs. J(J+1) for the H_2Se molecule. ($V_1 = V_2 = V_3 = 0$)

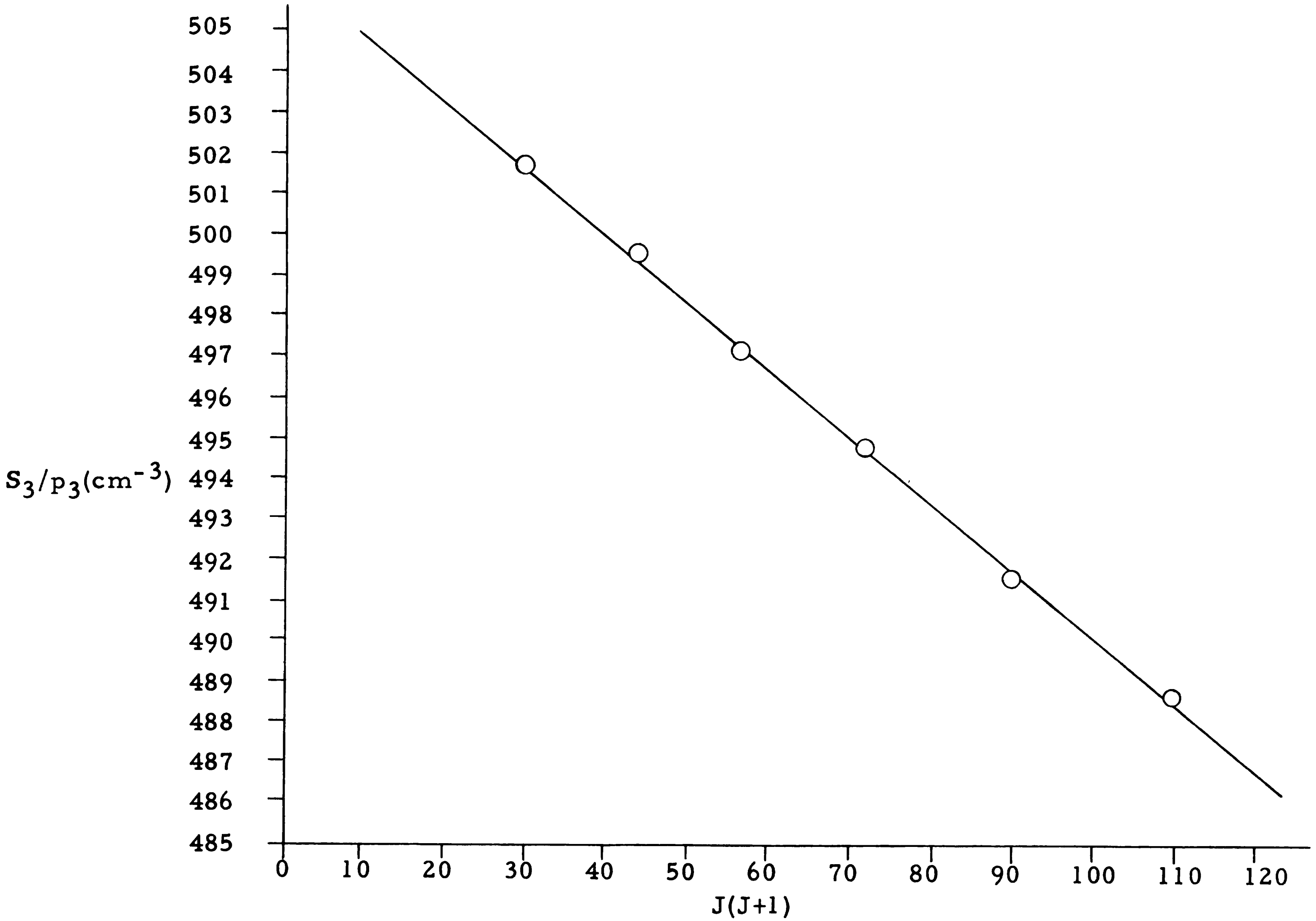

Figure 4. Plot of $-S_3/p_3$ vs. J(J+1) for the H_2Se molecule. ($V_1 = V_2 = V_3 = 0$)

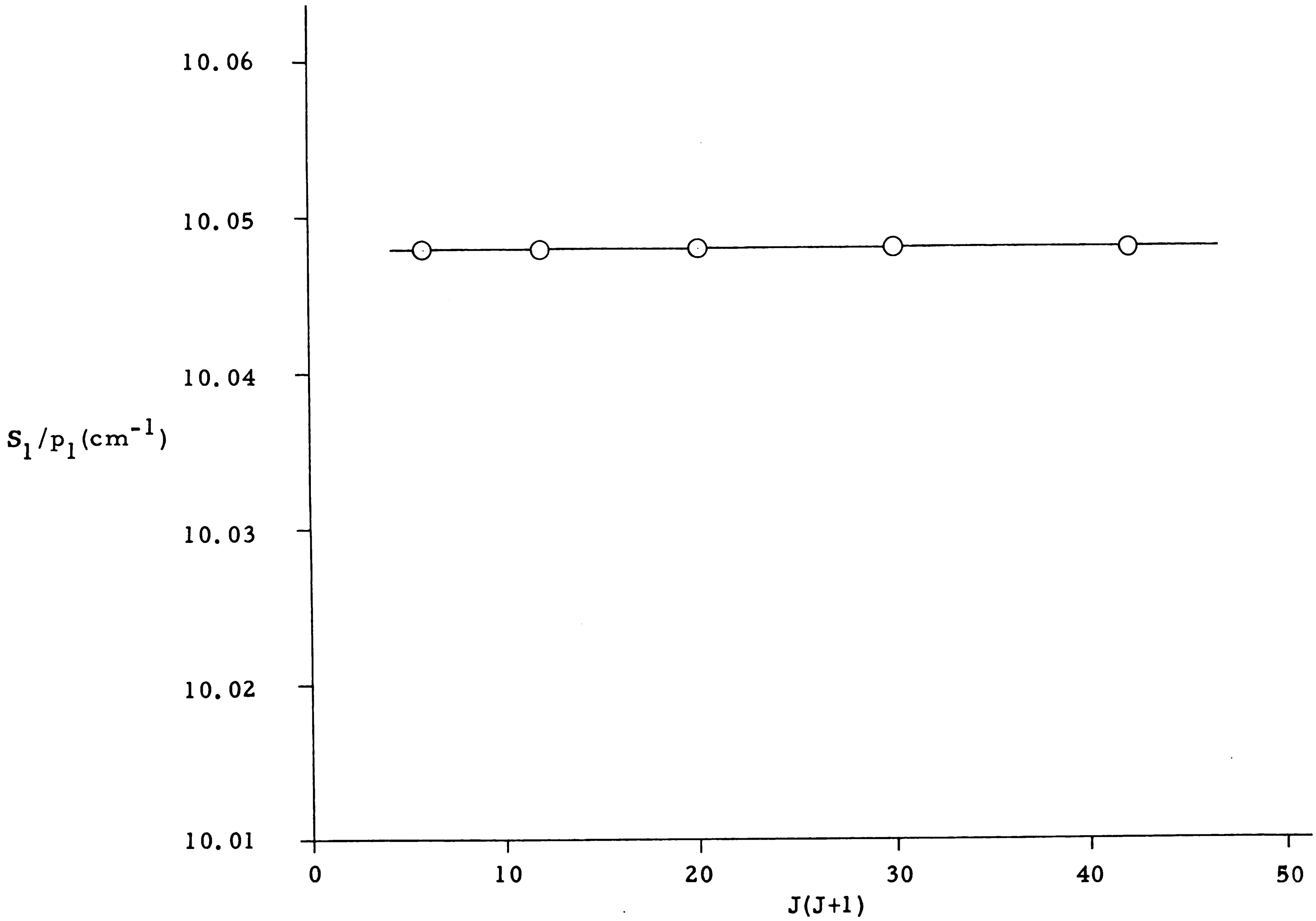

Figure 5. Plot of S_1/p_1 vs. J(J+1) for the D_2Se molecule. ($V_1 = V_2 = V_3 = 0$)

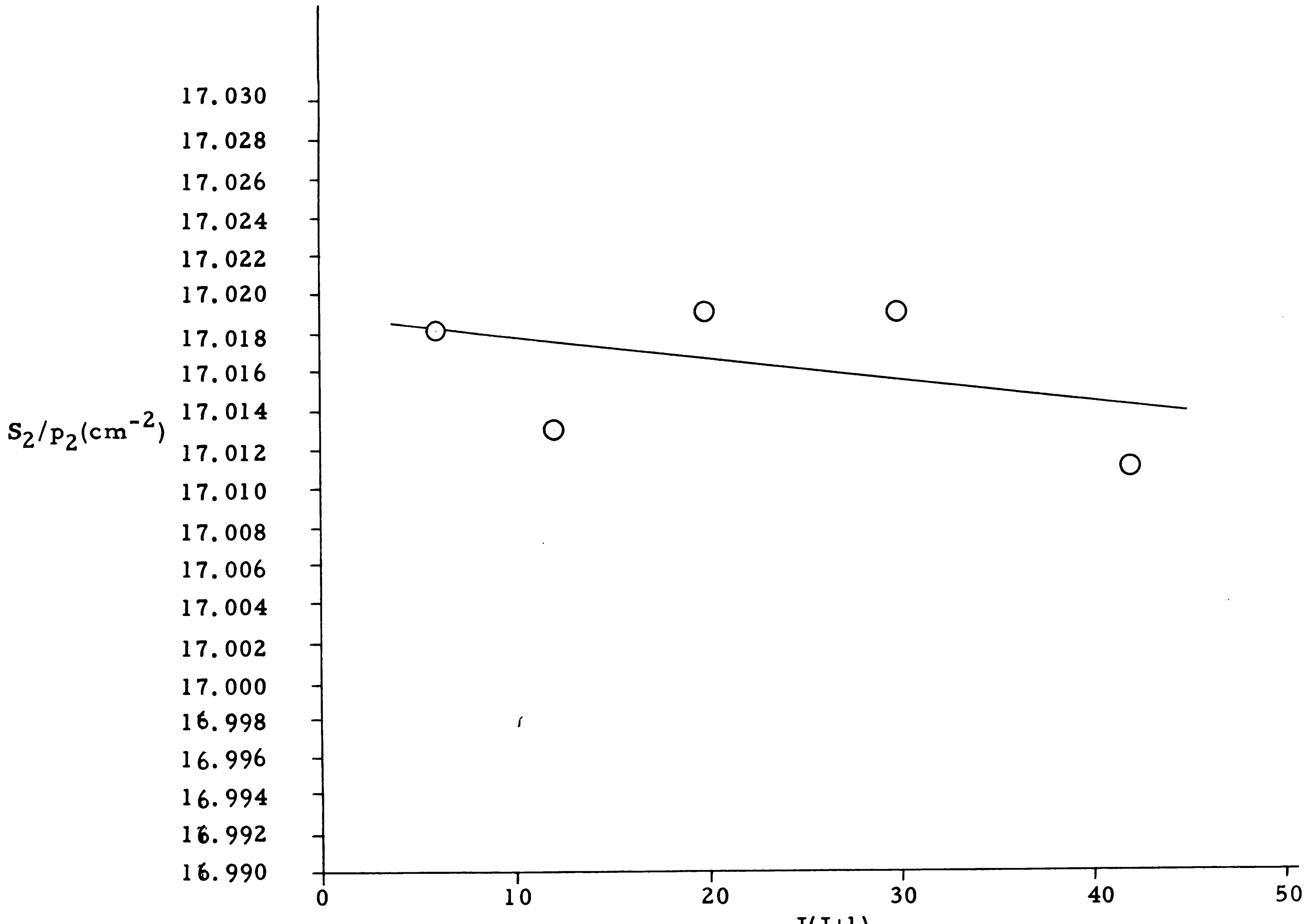

Figure 6. Plot of S_2/p_2 vs. J(J+1) for the D_2Se molecule. (V_1 - V_2 = V_3 = 0)

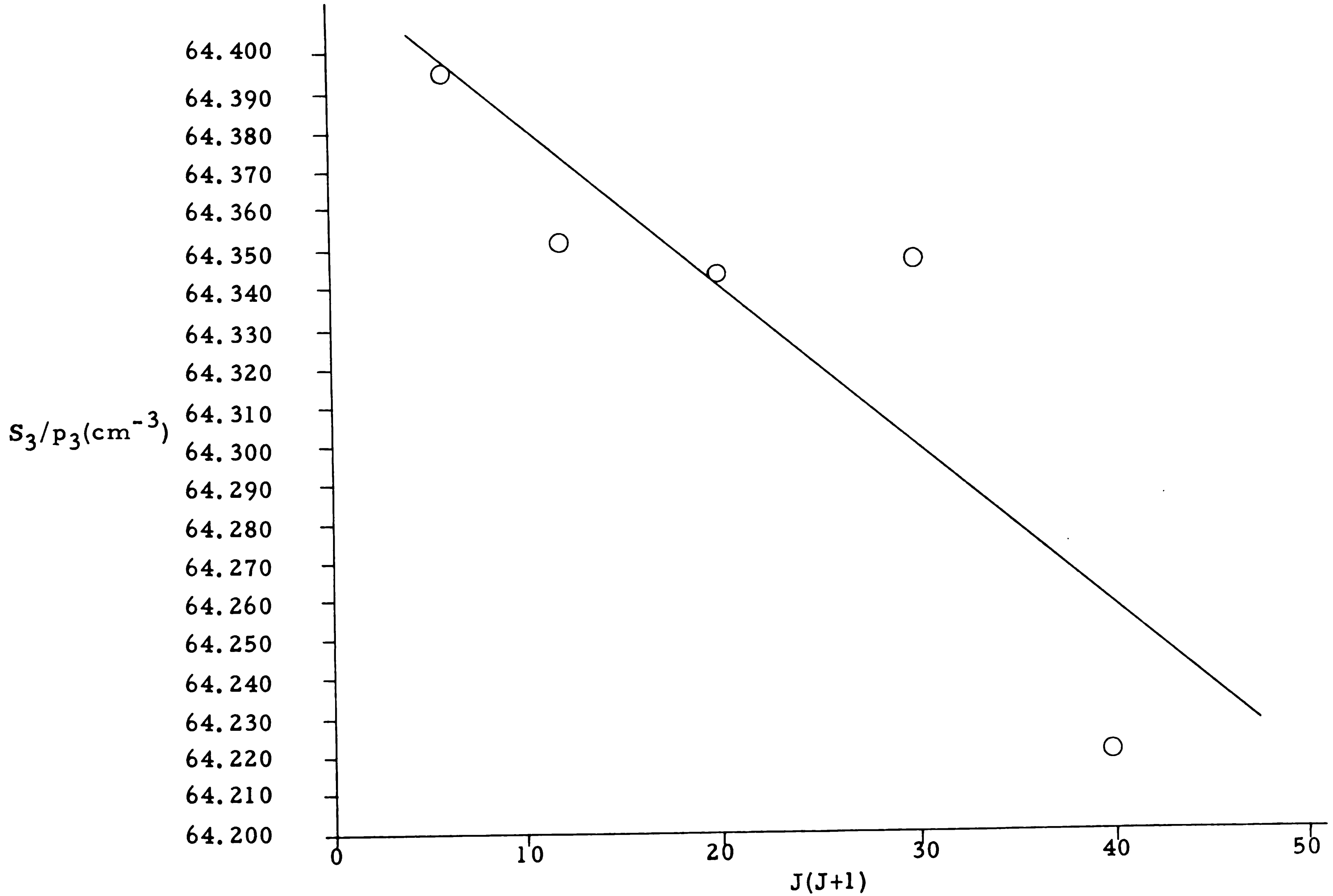

Figure 7. Plot of $-S_3/p_3$ vs. J(J+1) for the D_2Se molecule. ($V_1 = V_3 = V_2 = 0$)

Table IX - Parameters of H_2Se and D_2Se calculated from a rigid analysis of extrapolated values (to J=0) of S_i/p_i

H_2Se ($V_1 = V_2 = V_3 = 0$)

α	β	γ	A	B	C
19.795	.17032	8.0501	8.1683	7.7115	3.9150

D_2Se ($V_1 = V_2 = V_3 = 0$)

α	β	γ	A	B	C
10.048	.23758	4.0871	4.1924	3.8687	1.9870

α, γ, A, B, and C in units of cm^{-1}; β dimensionless.

A non-rigid analysis of these data then followed. By using the values of α, β, and γ obtained from the preceding rigid analysis along with the slopes of the curves from equations (3.1) through (3.6) it was possible to find α_1, γ_2, and β_2 from (2c.6), (2c.17) and (2c.18). The values of α_2, β_1, and γ_1 then followed from the relations: $\alpha_1 = \alpha_2$, $\beta_1 = \beta_2$, and $\gamma_1 = -2\gamma_2$. The λ_i s were next determined from equations (2c.19) through (2c.24). Finally, the σ_i s were calculated by using (2.b7). The values of the stretching coefficients λ_i, and the resulting coefficients σ_i of the centrifugal correction terms in the Hamiltonian (2b.3) are listed in Table X.

Error Analysis

An error analysis[9] was performed in order to measure the quality of the fit obtained by the method of least squares for equations (3.1) through (3.6). As the final interest lies in the rotational constants and in the coefficients of the centrifugal correction terms, the probable error of the values used to calculate them were found. These values were the probable errors in the slopes and intercepts of equations (3.1) through (3.6); results are tabulated in Table XI.

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[9] F.A. Willers, Practical Analysis, Chapter IV, (Dover Publications, New York, 1948)

Table X - Stretching coefficients λ_i and centrifugal correction term coefficients σ_i

H_2Se ($V_1 = V_2 = V_3 = 0$)

λ_1	$+ 3.0498 \times 10^{-5}$	σ_1	$+ 1.8413 \times 10^{-3}$
λ_2	$- 3.8924 \times 10^{-5}$	σ_2	$- 2.3501 \times 10^{-3}$
λ_3	$- .91317 \times 10^{-5}$	σ_3	$- .55133 \times 10^{-3}$
λ_4	$- 2.4028 \times 10^{-5}$	σ_4	$- 1.4507 \times 10^{-3}$
λ_5	$+ 1.0684 \times 10^{-5}$	σ_5	$+ .64505 \times 10^{-3}$
λ_6	$- .42125 \times 10^{-5}$	σ_6	$- .25433 \times 10^{-3}$

D_2Se ($V_1 = V_2 = V_3 = 0$)

λ_1	$+ 2.1317 \times 10^{-6}$	σ_1	$+ 6.5344 \times 10^{-5}$
λ_2	$- 2.3160 \times 10^{-6}$	σ_2	$- 7.0994 \times 10^{-5}$
λ_3	$+ .18433 \times 10^{-6}$	σ_3	$+ .56504 \times 10^{-5}$
λ_4	$- 1.0658 \times 10^{-6}$	σ_4	$- 3.2671 \times 10^{-5}$
λ_5	$+ 1.1580 \times 10^{-6}$	σ_5	$+ 3.5497 \times 10^{-5}$
λ_6	$- .09217 \times 10^{-6}$	σ_6	$- .28252 \times 10^{-5}$

Table XI - Slopes and intercepts of equations (3.1) through (3.6) and the probable error in these values *

H_2Se ($V_1 = V_2 = V_3 = 0$)

	S_1/p_1	S_2/p_2	S_3/p_3
Intercept	19.795±.003	65.431±(.013)	-506.55±.09
Slope	$(-10.595\pm.052) \times 10^{-4}$	$(-210\pm1.92) \times 10^{-4}$	$(1632.2\pm12.1) \times 10^{-4}$

D_2Se ($V_1 = V_2 = V_3 = 0$)

	S_1/p_1	S_2/p_2	S_3/p_3
Intercept	10.048±.001	17.019±.002	-64.421±.02
Slope	0	$(-1.261\pm.8363) \times 10^{-4}$	$(40.8\pm7.95) \times 10^{-4}$

* S_1/p_1 in units of cm^{-1}, S_2/p_2 in units of cm^{-2}, S_3/p_3 in units of cm^{-3}

These values of S_i/p_i along with their probable errors were used in a rigid analysis once more to determine α, β, and γ. The worst possible combinations of these values and their corresponding probable errors were used this time in order to ascertain the largest error that might result in the present calculations. These "worst" values of α, β, and γ were next used in the same manner to determine the rotational constants in the way previously described. Results showed that A and B for the H_2Se molecule might be in error as much as $\pm .01$ cm^{-1} and the value of C by as much as $\pm .02$ cm^{-1}.

An error analysis of the stretching coefficients was carried out in the same manner. Here, the slopes of the S_i/p_i curves along with their probable errors were used in conjunction with the "worst" values of α, β, and γ to find the greatest error likely to occur in the stretching coefficients λ_i. The λ_i s were in turn used to determine the greatest amount by which the coefficients σ_i might be in error. The results of the calculations are shown in the summary in Table XII.

IV

Summary

The "unstretched" values of the rotator constants A, B, and C obtained by the energy moment method in the present work are in very close agreement with the values which Palik and Oetjen[7] arrived at by employing a different method of analysis. A comparison of the results is shown in Table XIII.

The coefficients of the centrifugal correction terms in the Hamiltonian seem to be reasonably accurate for H_2Se; Table XII shows that the values calculated from these data might be in error by as much as $\pm .04 \times 10^{-3} cm^{-1}$.

Although the values of the rotational constants for D_2Se are quite satisfactory, the results obtained for the σ_i s are rather poor; the error may be as high as 28%. D_2Se is not a very "stretchy" molecule; the zero slope of equation (3.4) and the very small slopes of the curves represented by equations (3.5) and (3.6) bear this out. As a consequence, a small error in the calculated value of the slope shows up in the end results as a very large relative error.

In this particular case it is believed that the data, although sufficient to enable determination of the rotator con-

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[7] E.D. Palik and R.A. Oetjen, J. Molecular Spectroscopy, 3, 259, (1959)

Table XII - Coefficients of the centrifugal correction terms in the Hamiltonian - equation (2b. 3)

H_2Se $(V_1 = V_2 = V_3 = 0)$

$$\sigma_1 = (+1.84_1 \pm .010) \times 10^{-3}$$

$$\sigma_2 = (-2.35_0 \pm .002) \times 10^{-3}$$

$$\sigma_3 = (-.551_3 \pm .002) \times 10^{-3}$$

$$\sigma_4 = (-1.45_1 \pm \ 000) \times 10^{-3}$$

$$\sigma_5 = (+.645_0 \pm .010) \times 10^{-3}$$

$$\sigma_6 = (-.254_3 \pm .040) \times 10^{-3}$$

D_2Se $(V_1 = V_2 = V_3 = 0)$

$$\sigma_1 = (+6.53_4 \pm 1.84) \times 10^{-5}$$

$$\sigma_2 = (-7.09_9 \pm 1.79) \times 10^{-5}$$

$$\sigma_3 = (+.565_0 \pm .05) \times 10^{-5}$$

$$\sigma_4 = (-3.26_7 \pm 1.10) \times 10^{-5}$$

$$\sigma_5 = (+3.55_0 \pm .89) \times 10^{-5}$$

$$\sigma_6 = (-.282_5 \pm .11) \times 10^{-5}$$

Table XIII - Rotational constants of H_2Se and D_2Se for the vibrational* state ($V_1 = V_2 = V_3 = 0$)

	Present work		Palik and Oetjen**
	H_2Se		**H_2Se**
A	8.16_8	A	8.16_5
B	7.71_1	B	7.71_2
C	3.91_5	C	3.91_5
	D_2Se		**D_2Se**
A	4.19_2	A	4.19_3
B	3.86_9	B	3.86_5
C	1.98_7	C	1.98_7

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* All values expressed in units of cm^{-1}.

** These values for the rotational constants are taken from the works of Palik and Oetjen[7] where it is stated that they may be in error by as much as ± .02 cm^{-1}.

[7] E.D. Palik and R.A. Oetjen, J. Molecular Spectroscopy, 3, 259, (1959).

stants with a fair degree of accuracy, is insufficient to obtain the slope of the S_i/p_i vs. $J(J+1)$ curve accurately enough. Figs. 5, 6, and 7 show the graphs of these data for D_2Se. Here it is seen that although the data for the S_i/p_i curve is satisfactory, the data for the S_2/p_2 and S_3/p_3 are very limited and very erratic. Inclusion of a value of S_i/p_i which may border on the point of rejection, while it may not change the value of the intercept appreciably, can result in a relatively large change in the slope of the curve. The smaller the slope of the curve, the more sensitive the values of σ_i would be to such a change. Without doubt, acceptable results could be obtained had more complet e data been available for the D_2Se molecule.

The data for the higher vibrational states is seen to be far too limited and erratic to warrant any attempt at analysis beyond the calculation of the effective values of the rotational constants obtained by a rigid analysis.