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Contents

ROTATIONAL PERTURBATIONS AND LOW-LYING ELECTRONIC STATES OF CaO

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ABSTRACT

Sixteen bands of the $A^1\Sigma - X^1\Sigma$ transition of CaO^{18} were analyzed. They are the (6,3), (5,2), (5,3), (4,1), (4,2), (3,0), (3,1), (3,2), (2,0), (2,1), (2,3), (1,0), (1,1), (1,2), (0,0), and (0,1) bands. The spectroscopic constants found are:

$X^1\Sigma$	$A^1\Sigma$
$\omega_e = 702.18$	$\omega_e = {\sim}686.5$
$\omega_e x_e = 4.29$	$\omega_e x_e = {\sim}1.5$
$B_e = .4093$	$B_e = .3733$
$\alpha_e = .003$	$\alpha_e = .0009$
$D_e = {\sim}5.24\times10^{-7}$	$D_e \cong 4.58\times10^{-7}$
$\beta_e = {\sim}5.9\times10^{-8}$	

$$\nu_{0,0} = 11548.6$$

Thirty-seven perturbations were found in the upper state. They are due to six electronic states or substates. A comparison of these perturbations with those found in CaO^{16} (Hultin and Lagerqvist, 1950) indicates that four of these perturbing states lie below the $X^1\Sigma$, one is at ~8080 cm^{-1} and one is the $X^1\Sigma$ state.

I. INTRODUCTION

Previously analyzed spectra have shown four electronic states of CaO: $X^1\Sigma(0.0)$, $A^1\Sigma(\sim 11500\ cm^{-1})$, $B^1\Pi(\sim 25900\ cm^{-1})$ and $C^1\Sigma(\sim 28800\ cm^{-1})$. (Lagerqvist, 1954; Hultin and Lagerqvist, 1950) However, a comparison of the electronic states of the eight-electron isoelectronic molecules and their trends in energy (Brewer, 1962), indicates low-lying $^3\Pi$, $^3\Sigma$ $^1\Pi$ and $^1\Delta$ states. There are also experimental indications that unanalyzed low-lying electronic states exist. First, the spectra of CaO contains several regions (5555 Å, 6100 Å) of very dense, complex structure which have so far resisted a complete analysis. (Gaydon, 1955; Kobajiehok and Sokolov, 1968) It is possible that they are due to triplet states of CaO. Other possibilities include Ca_2O_2, CaOH and Ca_2. Second, the Birge-Sponer extrapolation of the $X^1\Sigma$ state gives 37 kcal for the dissociation energy. This value is at least 45 kcal lower than those obtained by other methods (Gaydon, 1968) which suggests that either $X^1\Sigma$ is not the ground state or that the extrapolation is anomalous. Third, some 30 rotational perturbations have been found in the $A^1\Sigma$ state of CaO. (Hultin and Lagerqvist, 1950). They have been explained as interactions between $A^1\Sigma$ and six other states or substates. The absolute vibrational numbering of these perturbing states, and hence their origins, were not obtained since the $v' = 0$ level of $A^1\Sigma$ was perturbed. All that can be deduced from the CaO^{16} data is that at least 6 electronic states or substates lie below 11500 cm^{-1}.

It would be helpful to know the relative energies of these perturbing states especially since some of them are predicted to be triplets.

No triplet state has been directly analyzed in CaO and there is some controversy on whether the ground state is a singlet or a triplet. The statistical weight of the ground and low-lying electronic states is important in thermochemical calculations. For example in calculating the dissociation energy by a third law method (T = 2000°K), a difference of 7 kcal/mole is obtained depending on whether the ground state of CaO is $^1\Sigma$ or $^3\Pi$ (Gaydon, 1968).

Before we consider a way of determining these relative energies, a word is in order concerning rotational perturbations. A rotational perturbation is an interaction between rotational energy levels. Theoretically, it is a mixing of wavefunctions, the Hamiltonian being cross-terms not considered in the Born-Oppenheimer approximation. Experimentally it is seen as a shift of rotational energy levels away from their otherwise regular spacing. The following selection rules should hold in order for a rotational perturbation to occur:

(1) Both states must have the same total angular momentum, J, at approximately the same energy; $\Delta J=0$, $\Delta E\sim 0$.

(2) Both states must have the multiplicity; $\Delta S=0$.

This rule holds only approximately (Ballik and Ramsey, 1962)

(3) $\Delta\Lambda = 0,\pm 1$ for Hund's coupling cases (a) and (b)

$\Delta\Omega = 0,\pm 1$ for Hund's case (c)

(4) Both states must be positive, or both must be negative; $+ \not\leftrightarrow -$

(5) For identical nuclei, both states must have the same symmetry in the nuclei; $s \not\leftrightarrow a$

(6) There must be sufficient overlap of the vibrational eigenfunctions.

More thorough discussions of rotational perturbations can be found in Herzberg, Spectra of Diatomic Molecules, 1965, and Kovacs, Rotational Structure in the Spectra of Diatomic Molecules, 1969.

A standard method of assigning vibrational numbers, v, is to observe the isotopic shift of the vibrational levels according to formula (1):

$$\text{SHIFT} = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 - \rho\omega_e(v + \tfrac{1}{2}) + \rho^2\omega_2 x_e(v + \tfrac{1}{2})^2 \qquad (1)$$

where $\rho = \sqrt{\mu/\mu_i}$, and μ is the reduced mass. The higher the v-number, the greater the shift, until the $\omega_e x_e$ terms become dominant. A similar method can be used with the six states perturbing the $A^1\Sigma$ state. A perturbation can occur when two (or more) vibrational levels (from different electronic states) have approximately the same energy at the same rotational quantum number, J($\Delta E \sim 0$, $\Delta J = 0$). Therefore on a plot of energy vs J(J+1), a perturbation is possible where the lines representing the two vibrational levels cross (see Fig. 1). When a heavier isotope is used these levels shift downward in energy as indicated by formula (1) and intersect one another at a new energy and J value. (The isotopic-effect on the rotational constants is ignored in this example for simplicity. It would change the slope of the lines slightly.) The amount of the shift, and hence the position of the perturbation, is dependent upon which vibrational levels are involved. Thus a comparison of the perturbations in the $A^1\Sigma$ state of CaO^{16} and CaO^{18} should help clarify the relative energies of the six perturbing states. With this end in mind the spectrum of CaO^{18} in the region of 7200 Å to 9400 Å ($A^1\Sigma$-$X^1\Sigma$ system) was taken and analyzed.

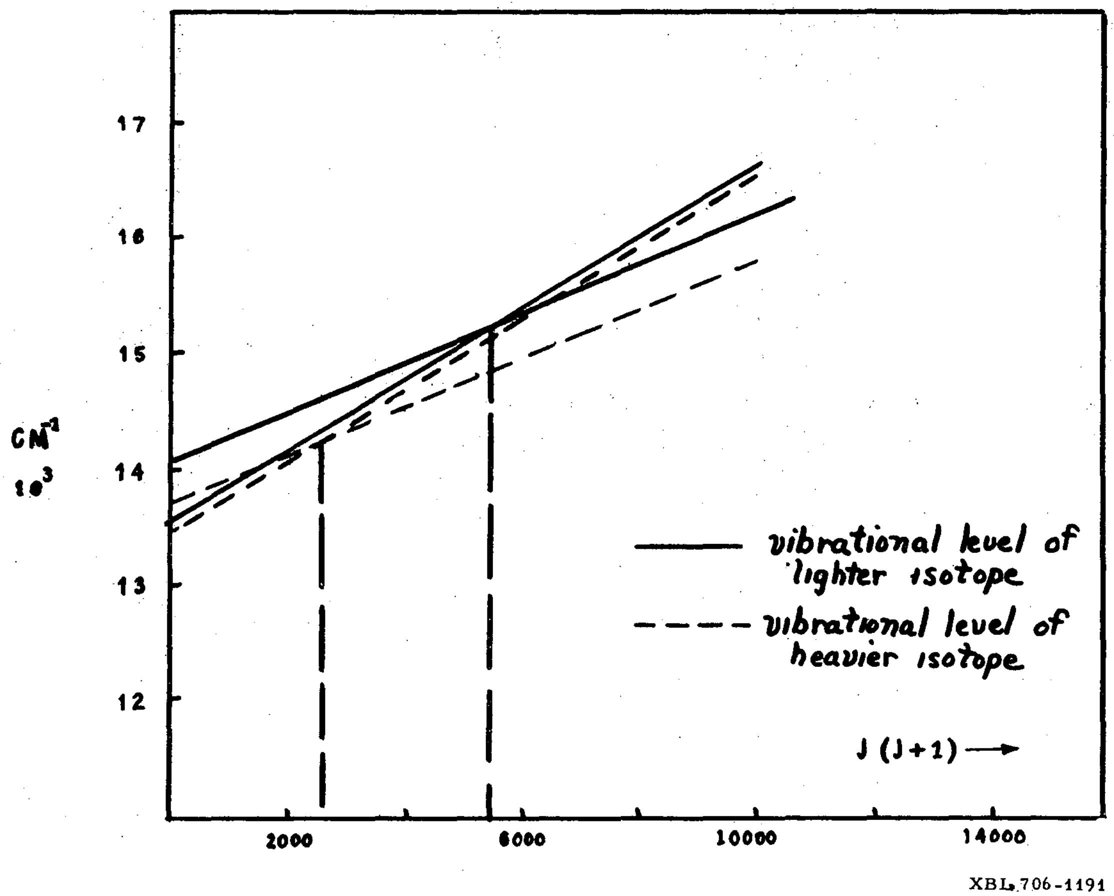

Fig. 1. Plot of energy vs J(J+1) showing how a rotational perturbation shifts with a change of isotope.

II. EXPERIMENTAL

The light source used was a reduced pressure arc operated by a 300 volt d.c. power supply at a current of 1 amp (Hauge, 1965) (Figs. 2 and 3). The electrode-holders were water-cooled and held calcium rods one-fourth inch in diameter. The arc was initiated with a Tesla coil and run at a pressure of 1 torr of He gas and ~ 0.3 torr of O_2^{18}. Oxygen was added to the system as it was used up at regular intervals. A P_2O_5 trap was used to absorb water vapor. Before new electrodes were used, their tips were first scraped clear of CaO.

The spectrograms were taken in the first order of a 1.5 meter. Jarell Ash grating spectrograph(1180 grooves/mm). Exposure times ran from 15 min to 1 hr. Eastman Kodak IN and IM plates were used; the IM plates were hypersensitized first with ammonia.* A Kodak Wratten gelatin filter No. 89B was also used. The dispersion was 4.4 Å/mm; resolution approximately 0.1 cm^{-1}. A thorium electrodeless discharge tube generated the standard lines. (A neon Osram lamp was used in the 9000 Å-9400 Å region to identify the Th lines.)

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*The hypersensitizing procedure was obtained from Dr. Sumner Davis and is as follows:

(1) Four minutes in a solution of 6% ammonium hydroxide at 40°F

(2) One minute in a solution of one part isopropyl alcohol, two parts distilled water, and one cc of glacial acetic acid per one hundred cc of solution.

(3) Four minutes in a solution of two parts isopropyl alcohol and one part distilled water by volume.

(4) Dry the plate before storage or use. The plate should be stored in the freezer and used within two weeks.

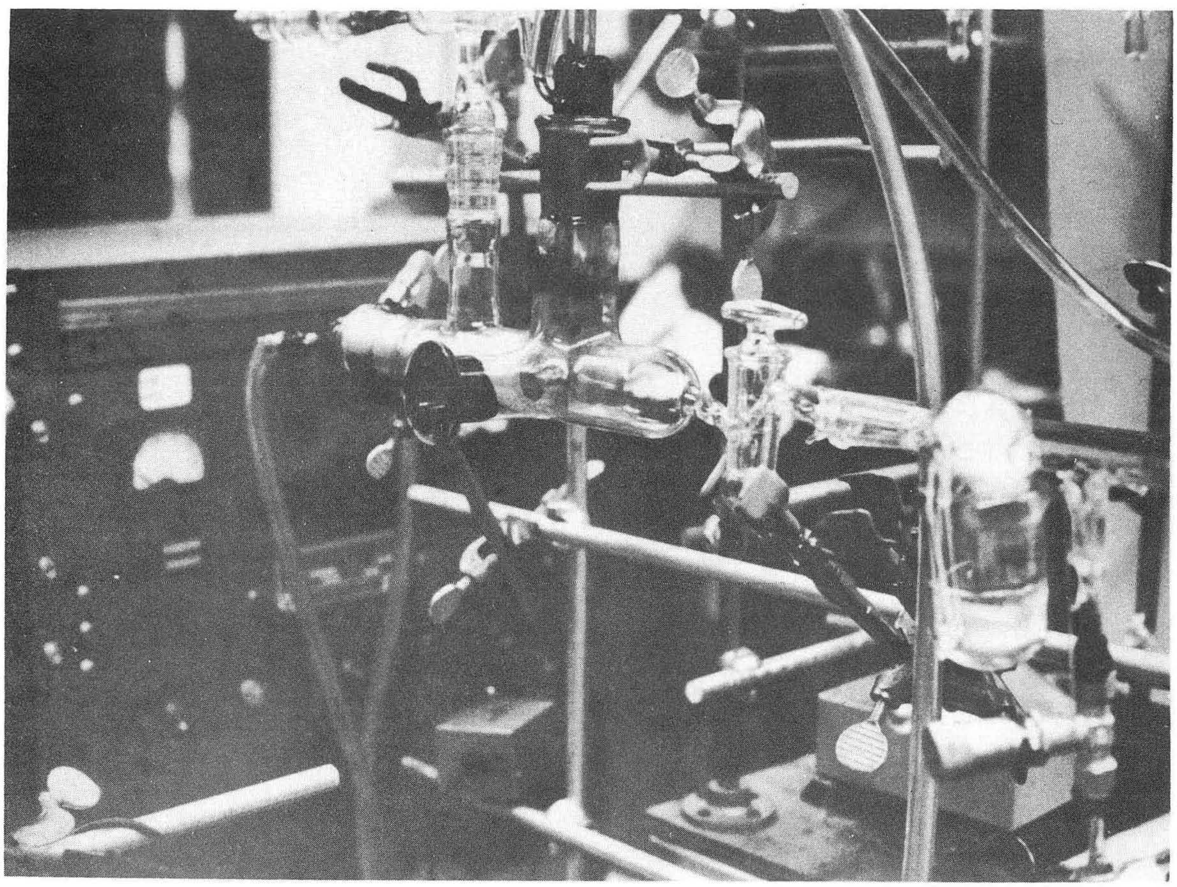

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Fig. 2. Photograph of arc.

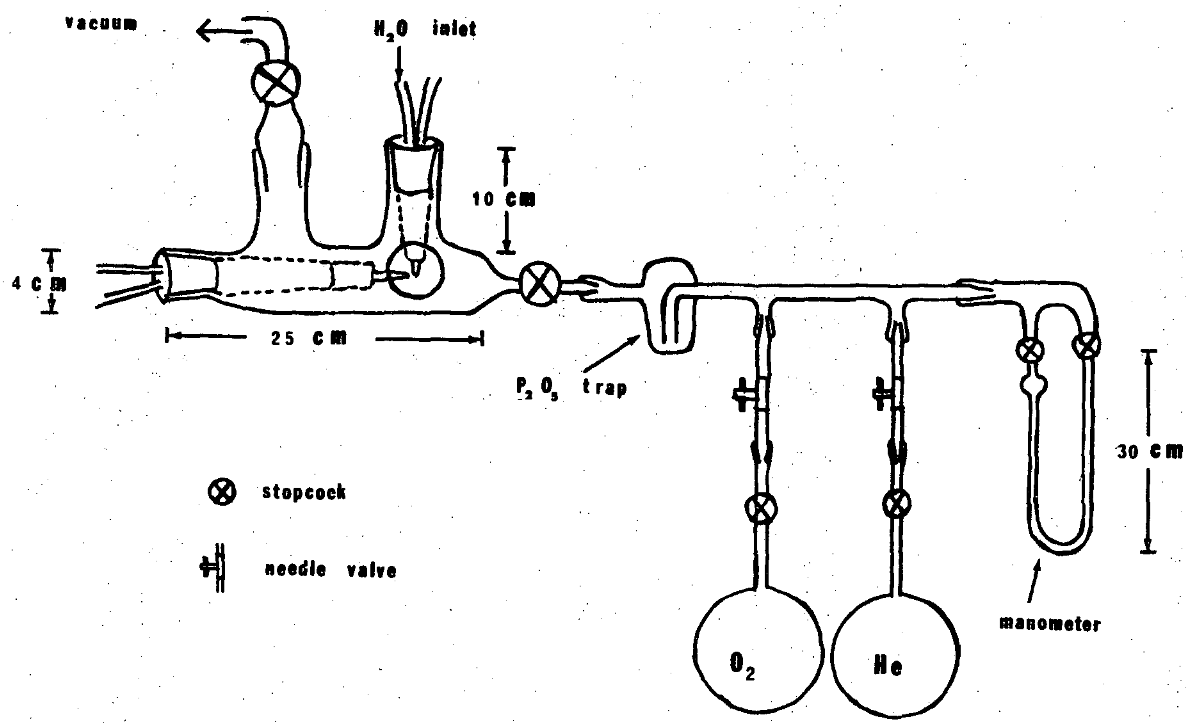

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Fig. 3. Schematic of vacuum system.

III. RESULTS

A. Analysis

Five red-degraded sequences appeared in the CaO spectrum at approximately 7300, 7700, 8150, 8650, and 9200 Å. Analysis has shown them to be respectively the (3,0), (2,0), (1,0), (0,0), and (0,1) sequences of the $A^1\Sigma-X^1\Sigma$ transition of CaO^{18}. There was no problem with contamination by O_2^{16}. However strong atomic lines blotted out part of the (2,0) and (0,0) sequences. Weak exposures were taken in these regions to pick up as many CaO^{18} lines as possible (see Figs. 4, 5, 6, 7).

Sixteen bands were analyzed: (0,0), (0,1), (1,0), (1,1), (1,2), (2,0), (2,1), (2,3), (3,0), (3,1), (3,2), (4,1), (4,2), (5,2), (5,3), and (6,3). Perturbations have been found in the upper level of each of these bands. See Table 2 for a listing of the assigned lines. Two columns are given for both the R- and P- branches. A shift from one column to the other indicates a perturbation. M's stand for missing lines, A's for lines that have been obscured by an atomic line, and H's for lines obscured by band heads.

The analysis itself was accomplished by calculating the combination differences, $\Delta_2F''(J)$, of the $X^1\Sigma$ vibrational levels using ρ and the spectroscopic constants of CaO^{16} (Hultin and Lagerqvist, 1950). The spectrum was then scanned by computer for sets of lines which satisfied these combination differences and the results were plotted out (Kopp, et al. 1965).

$$\Delta_2F''(J) = R(J-1) - P(J+1) = F_v''(J+1) - F_v''(J-1) \qquad (2)$$

R(J) and P(J) refer to the indicated J lines in the R and P branches and $F_v''(J)$ is the energy of the J-rotational level of the lower vibrational state. A more detailed explanation and a listing of the computer program is found in Appendix B.

B. Determination of Rotational Constants

The rotational constants of the unperturbed $X^1\Sigma$ vibrational levels were determined by plotting $\Delta_2F''(J)/4(J+\frac{1}{2})$ vs $(J+\frac{1}{2})^2$ where

$$\Delta_2F''(J) = R(J-1)-P(J+1) = 4B_v''(J+\tfrac{1}{2}) - 8D_v''(J+\tfrac{1}{2})^3 \qquad (3)$$

A sample plot is found in Appendix B and the rotational constants, B_v'' and D_v'' in Table 3.

The corresponding plot for the upper-state levels (i.e. $\Delta_2F'(J) = R(J) - P(J)$) fluctuated greatly due to the perturbations and could only give very approximate B-values. However, for such strongly perturbed levels it is meaningless to speak of a fixed B -value since every rotational level has a B -value which is a mixture of the B_v-values of the perturbed and perturbing states. One can however obtain a good approximation to the "unperturbed" B_v values by plotting $T/4J$ vs J^2 where:

$$\frac{T}{4J} = \frac{R(J-2)-R(J-1)+P(J)-P(J+1)}{4J} = B''-B' + 6D'' - 2J^2(D''-D') \qquad (4)$$

This gives $(B_v''-B_v')$ as the intercept at J=0. Using the B_v'' values found with Eq. (3), the B_v' values are easily calculated. The D_v' constants were obtained from the unperturbed sections of a plot of $\Delta_2F'(J)/4(J+\frac{1}{2})^2$. Their average is found in Table 4.

The calculated B-values in Table 3 are from the equations:

$$B_v'' = 0.4093 - 0.003(V+\tfrac{1}{2})$$
$$B_v' = 0.3733 - 0.0009(V+\tfrac{1}{2}) \qquad (5)$$

C. Determination of Vibrational Constants

The band origins, ν_0, were determined in two ways. The first was the usual plot of $[(R(J-1)+P(J))/2]$ vs J^2

$$R(J-1) + P(J) = 2\nu_0 + 2(B'-B'')J^2 \qquad (6)$$

The second method was to plot the left-hand side of Eq. (7) vs J.

$$B_v'' - \frac{1}{4}\{J(J+1)[P(J)+R(J-2)] - (J-1)[P(J+1)+R(J-1)]\} = \nu_0 \qquad (7)$$

Both of these methods however could only give approximate values of ν_0 since the upper state is highly perturbed. For example, the V' = 1 level is shifted $\sim 8\ \text{cm}^{-1}$.

In order to calculate the vibrational constants of the unperturbed lower state, the influence of the upper state was subtracted out as follows (Hultin and Lagerqvist, 1950). Equation (6) was written for the two bands with the same upper level but with different lower levels a and b.

$$[R(J-1) + P(J)]_{v',v_a''} = 2\nu_0(v',v_a'') + 2(B'-B_a'')J^2 \qquad (8)$$

$$[R(J-1) + P(J)]_{v',v_b''} = 2\nu_0(v',v_b'') + 2(B'-B_b'')J^2 \qquad (9)$$

The difference between Eqs. (8) and (9), A, is

$$\begin{aligned} A &= 2[\nu_0(v',v_a'') - \nu_0(v'v_b'') + 2(B_b''-B_a'')J^2 \\ &= 2[G''(v_b'') - G''(v_a'')] + 2(B_b'' - B_a'')J^2 \end{aligned} \qquad (10)$$

where $G''(v_a'')$ is the energy of the v_a'' vibrational level of the lower state at J=0. The quantity A/2 is plotted vs J^2 to obtain $[G''(v_b'')-G''(v_a'')]$ as intercept and $[B_b'' - B_a'']$ as slope. The values obtained were very close to those calculated for CaO^{18} from the CaO^{16} spectroscopic constants given by Hultin and Lagerqvist (1950). The ω_e and $\omega_e x_e$ constants calculated from the $[G''(v''_b) - G''(v''_a)]$ values are found in Table 4.

Using these $[G''(v''_b) - G''(v''_a)]$ differences, a consistent set of band origins were picked out of the results of Eqs. (6) and (7). They are given in the Deslandre's Table of Table 1. These origins and the calculated intercepts at J=0 of the lower state vibrational level were used to calculate the energies of the upper state vibrational levels and the average values of these energies were in turn used to obtain the upper state vibrational constants (Table 3).

D. Perturbations in CaO^{18}

The 37 perturbations found in the $A^1\Sigma$ state of CaO^{18} are listed in Table 5. They can be assigned to six perturbing states: Z^{18}, Q^{18}, Y^{18}, W^{18}, X^{18}, and B^{18}. On the plot of energy vs J(J+1) in Fig. 14, the solid lines represent the first seven vibrational levels of the $A^1\Sigma$ state and the squares show the perturbations. The circles indicate the end of the analysis for that particular level and in all probability another perturbation. The dashed lines connect perturbations arising from the same perturbing state. In Table 5 the relative vibrational numbering for the perturbing states is given in column v_p, with the lowest levels of each state called X, Y, Z, Q, W, and B respectively.

In order to determine the B_v values of the perturbing levels, plots (Figs. 8-13) were made of T/4J vs J (see Eq. (4)) for all the analyzed bands. (Gerö, 1935; Kovacs, 1937; Hultin and Lagerqvist, 1950) For the unperturbed regions an almost horizontal line is obtained, while at a perturbation, two T/4J curves, F_1 and F_2, rise to a peak. Equations

(11) and (12) are applicable for these plots:

$$B_v^P = 2B_v'' - B_v' - 2S \qquad (11)$$

$$J_0 \sim J^* - \tfrac{1}{2} \qquad (12)$$

where S is the value of T/4J at which the curves F_1 and F_2 cross and J^* is the J value at this point, J_0 is the J value at which the perturbation culminates, B_v^P is the B value of the perturbing state, B_v' the B values of the $A^1\Sigma$ state, and B_v'' the B value of the $X^1\Sigma$ state. A proof of these equations is found in Kovacs (1937). The B_v^P values are listed in Table 5. They compare quite well with the expected values calculated from Eq. (13)

$$B_v^i = \rho^2 B_v \qquad (13)$$

where

$$\rho^2 = 0.9204$$

$$B_v^i = B_v \text{ for } CaO^{18}$$

$$B_v = B_v \text{ for } CaO^{16}$$

Lagerqvist and Hultin obtained $B_v \sim 0.33$ for the X^{16}, Y^{16}, Z^{16} and Q^{16} states of CaO^{16} and ~ 0.38 for the B^{16} state. For CaO^{18}, $B_v \sim 0.308$ for the X^{18}, Y^{18}, Q^{18} and Z^{18} states and ~ 0.35 for B^{18}.

The error in the B_v^P values found by the above method depends on the number of comparison lines found at each perturbation, the quality of these lines (i.e. overlapped, well-defined), the number of bands in which the perturbation is found, whether or not there are nearby perturbations to distort the B_v values of the perturbed level, etc. Because of the difficulty in estimating this error, the G(v) values (where G(v) is the energy of the v-vibrational level at J=0) were obtained by a simple graphical procedure. Consider the (Y+1) level of Y^{18} as an example. As shown in Table 5, the (Y+1) level of Y^{18} interacts with $A^1\Sigma$ at two points, $v_{A'\Sigma} = 0$, $J_0 = 93.50$ and $v_{A'\Sigma} = 1$, $J_0 = 27.0$. If D_v is assumed to be small (or, since both isotopic states are treated in the same way, the effect of D_v should cancel), the (Y+1) vibrational level can be represented as a straight line on a graph of energy vs J(J+1) (Fig. 14). That straight line is determined by the two points of perturbation mentioned above. The slope of the line is equal to the B_v value for that level and is listed in Table 5 under B_v^P(slope). In both CaO^{16} and CaO^{18} the B_v^P(slope) values are ~ 0.02 lower than the B_v^P values.

Since the B_v values of the other vibrational levels of Y^{18} would be expected to be similar to that of the (Y+1) level, the Y^{18} state can be shown as a series of lines parallel to (Y+1) and cutting through the other Y^{18} perturbations. The dashed lines in Fig. 14 represent the Y^{18} state; the solid lines the $A'\Sigma$ state. This was done for all the perturbing states of CaO^{18} and CaO^{16}. The perturbations of CaO^{16} were first replotted using the bottom of the potential curve of the $X'\Sigma$ state as the zero of energy. This was done so that the CaO^{16} and CaO^{18} levels would have the same reference point and could be compared. The G(v) results are given in Table 6 and the vibrational levels are graphed in Figs. 17 to 20. For the Z^{18} and Q^{18} states, the dashed lines in Fig. 14 connecting the perturbations coming from the same state were extended and the points of probable perturbation found used in graphing.

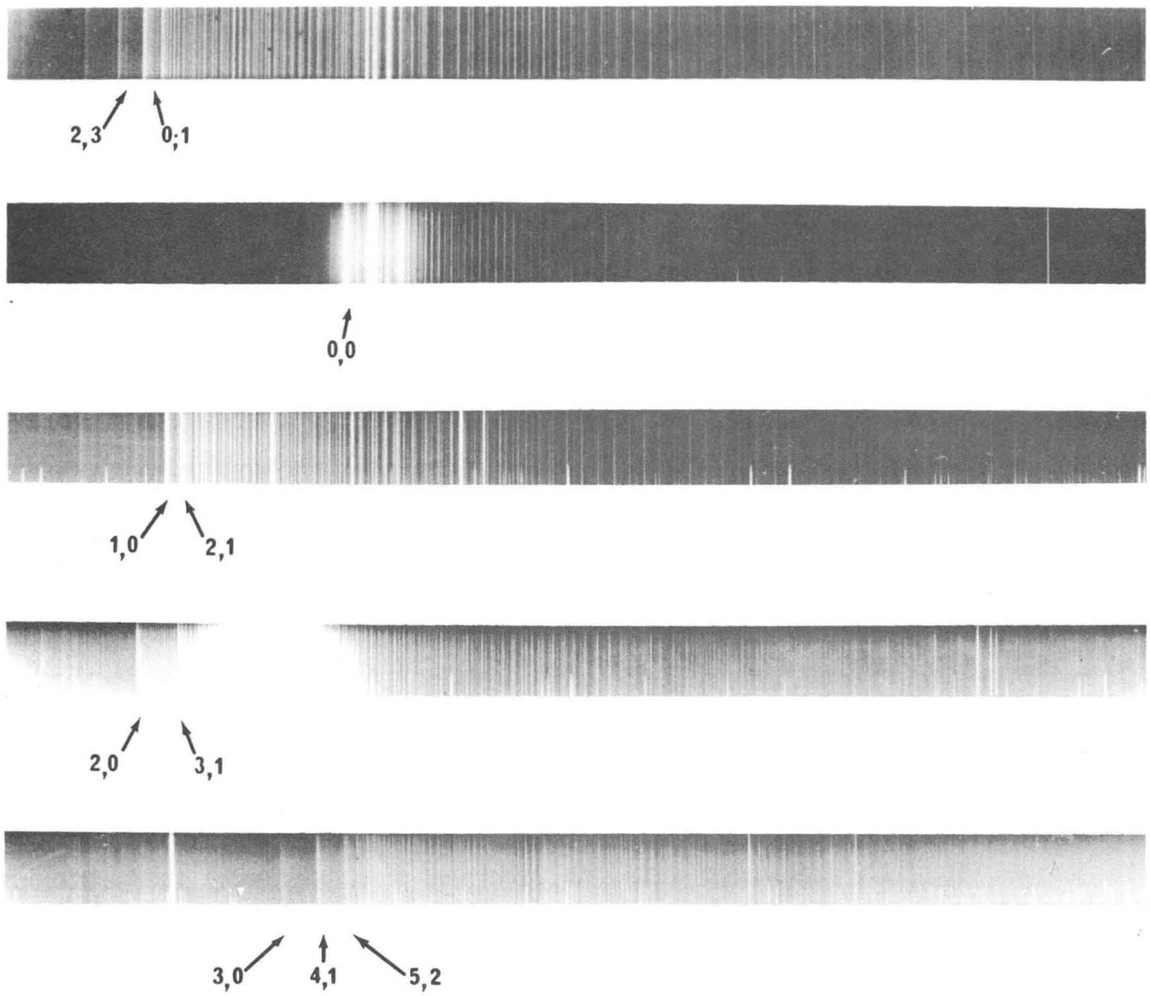

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Fig. 4. Spectrograms of the (0,0), (0,1), (1,0), (2,0), and (3,0) sequences of the A'Σ - X'Σ transition of CaO^{16}.

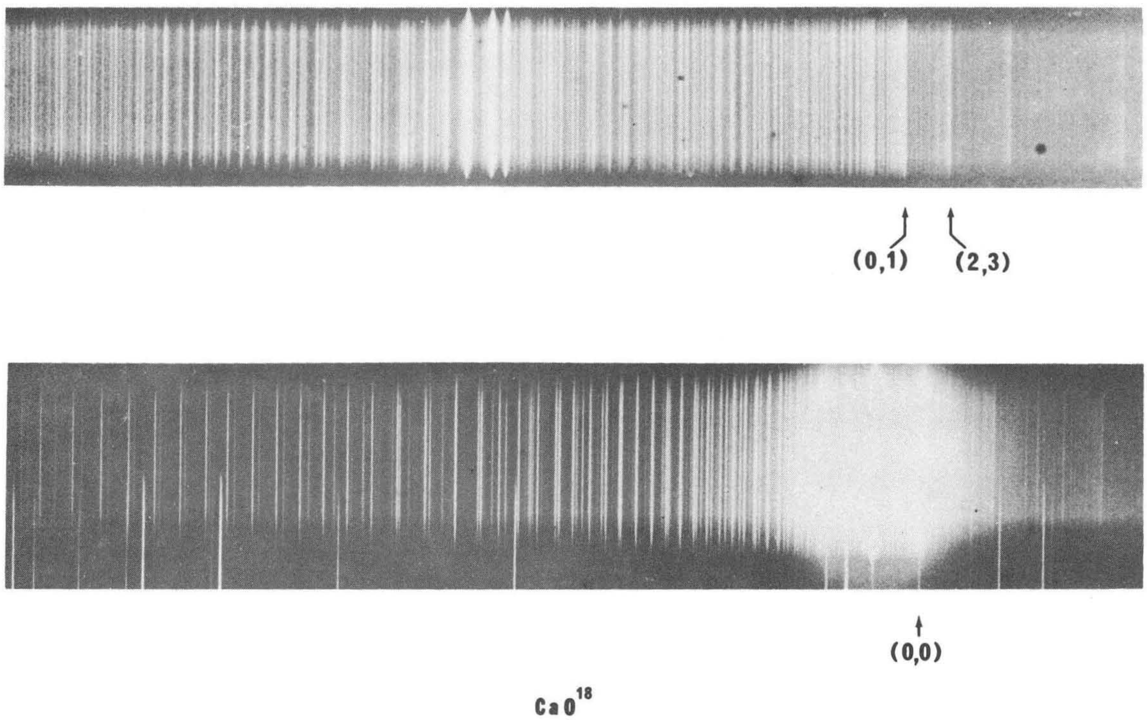

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Fig. 5. Reproduction of the (0,0) and (0,1) sequences.

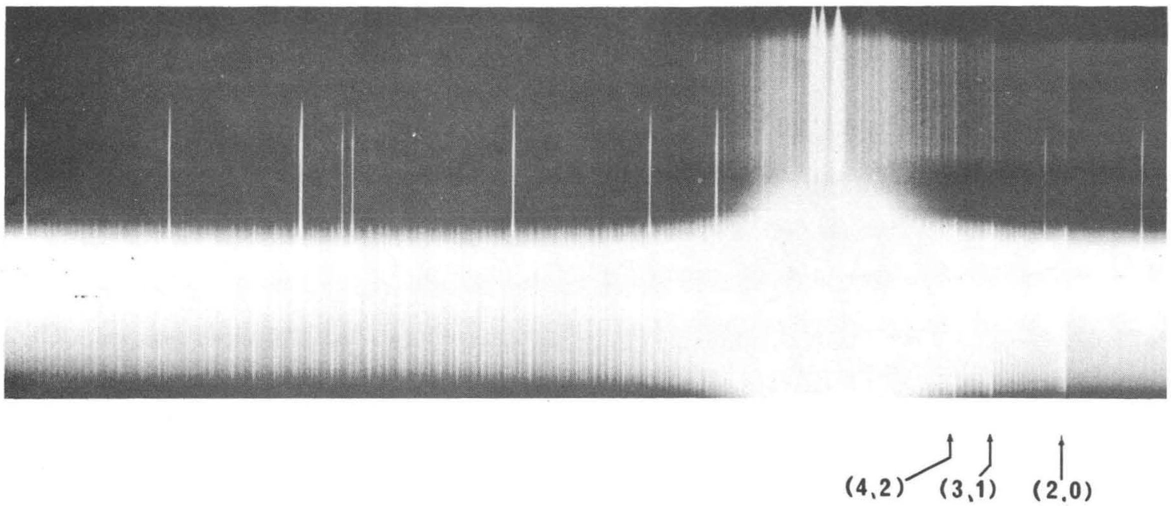

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Fig. 6. Reproduction of the (2,0) sequence.

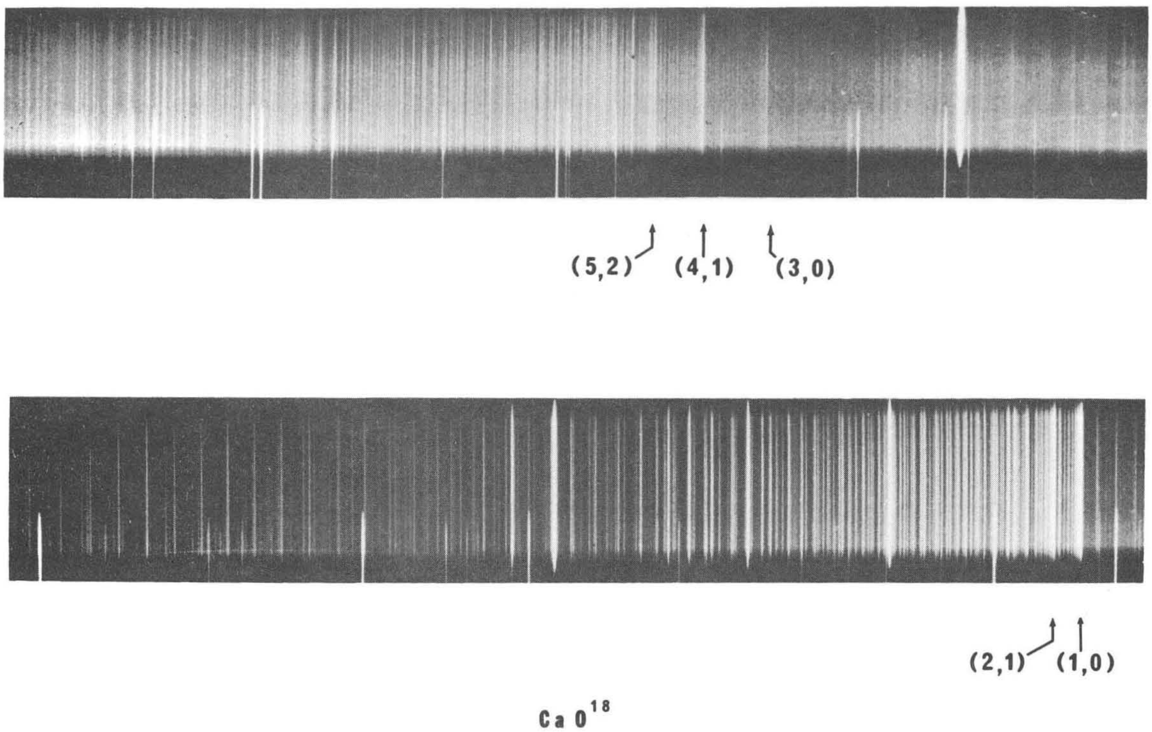

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Fig. 7. Reproductions of the (1,0) and (3,0) sequences.

Table 1. Deslandres Tables - Band Origins: CaO^{18}

↑ V' \ V'' →	0		1		2		3
6							13548.6
							666.9
5					13558.8	677.1	12881.7
					672.6		
4			13571.7	685.5	12886.2		
			673.7		674.9		
3	13589.7	691.7	12898.	685.7	12212.3		
	676.9		678.4				
2	12912.8	693.2	12219.6				10858.6
	674.8		679.2				
1	12238.5	689.1	11540.4	682.8	10857.6		
	689.9		687.6				
0	11548.6	695.8	10852.8				

Table 2. Listing of assigned lines in CaO^{18}

V'V''	0.	0.			0.	1.0		
J	P(J)		R(J)		P(J)		R(J)	
1								
2					10850.59			
3					10849.68			
4					10843.52			
5					10847.69			
6					10846.63			
7					10845.49			
8					10844.28			
9					10842.82			
10					10841.52			
11					10840.07			
12					10838.60			
13					10837.05			
14					10835.39			
15					10833.74			
16					10832.04			
17					10830.14		10856.38	
18					10828.30		10855.95	
19			11547.90		10826.33		10855.50	
20			11547.28		10824.39		10855.01	
21	11514.52		11546.58		10822.31		10854.45	
22	11512.25		11545.87		10820.24		10853.78	
23	11509.95		11545.00		10818.10		10853.13	
24	11507.60		11544.10		10815.79		10852.27	
25	11505.11		11543.06		10813.53		10851.52	
26	11502.65		A		10811.16		10850.59	
27	11499.93		A		10808.69		10849.68	
28	11497.26		11539.78		10806.21		10848.62	
29	11494.54		11538.41		10803.62		10847.43	
30	11491.72		11536.94		10800.97		10846.20	
31	11488.79		11535.51		10798.23		10844.92	
32	11485.78		11533.86		10795.36		10843.49	
33	11482.64		11532.04		10792.47		10841.86	
34	11479.40		11530.06		10789.44		10840.07	
35	11475.99		11527.79		10786.20		10837.93	
36	11472.39		11524.93		10782.86		10835.39	
37	11468.50		11521.45	11538.41	10779.52		10832.54	10847.26
38	11464.06		11516.73	11532.62	10774.86			10843.14
39	11458.94	11475.98		11528.92	10770.55	10785.15		10840.07
40	11452.75	11468.52		11525.82		10779.52		10837.05
41		11463.26		11523.10		10774.86		10834.59
42		11458.47		11520.63		10770.30		10832.17
43		11454.08		11517.96		10766.19		10830.14
44		11449.88		11515.50		10752.24		10827.77
45		11445.83		11512.99		10758.38		10825.64
46		11441.72		11510.43		10754.64		10823.25
47		11437.61		11507.62		10750.75		10820.79
48		11433.47	11505.52			10746.65	10818.96	
49		11429.08	11502.66			10742.76	10816.34	
50	11425.38		11499.95		10739.38		10813.90	
51	11420.94		11496.97		10735.29		10811.16	
52	11416.52		11493.84		10731.17		10808.50	
53	11411.96		11490.43		10726.91		10805.43	
54	11407.30		11486.43		10722.50		10801.79	
55	11402.29		11481.14	11493.01	10717.92		10796.78	10808.50
56	11396.72		11473.88	11486.42	10712.65			10802.18
57	11389.67	11401.75		11481.38	10705.00	10717.89		10797.67
58	11381.10	11393.43		11477.16		10710.07		10793,74
59		11386.99		11472.92		10703.92		A
60		11381.10		11458.52		10698.41		10785.94
61		11375.28		11463.43		10692.95		10781.12

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Table 2, continued.

V'V"	0.	0.			0.	1.0		
J	P(J)		R(J)		P(J)		R(J)	
62		11369.21	11473.31	11457.63		10687.23		10775.84
63		11362.65	11467.78	11450.57		10681.04	10786.58	10769.02
64	11370.93	11355.25	11461.88	11441.72		10673.99	10782.03	10760.45
65	11362.65	11346.65	11457.66		10683.41	10666.03	10778.38	
66	11356.40	11336.26	11452.75		10677.42	10656.29	10773.86	
67	11350.48		11445.33	11458.47	10672.13		10767.45	10778.38
68	11344.09			11452.63	10666.03			10772.93
69	11335.41	11348.32		11447.64	10658.20	10668.76		10766.47
70		11340.73		11443.19		10661.91		10764.42
71		A		11438.84		10655.91		10760.45
72		11328.24		11434.58		10650.33		10756.62
73		11322.35		11430.31		10644.85		10752.76
74		11316.52		11426.04		10639.45		10748.95
75		11310.70		11421.75		10634.06		10745.18
76		11304.87		11417.43		10628.74		10741.23
77		11299.02		11412.94		10623.32		10737.30
78		11293.11		11408.51		10617.85		10733.28
79		11287.17		11403.92		10612.40		10729.21
80		11281.15		11399.30		10606.86		10725.03
81		11275.05		11394.52		10601.25		10720.75
82		11268.84		11389.67		10595.53		10716.29
83		11262.55		11384.43		10589.75		10711.61
84		11256.05		11378.94		10583.74		10706.65
85		11249.38		11372.89		10577.58		10701.06
86		11242.33	11382.64	11365.64		10571.07		10693.73
87		11234.75	11367.27	11356.40		10563.96		10685.73
88	11243.06	11226.03	11357.95			10555.21		
89	11226.03	11215.29	11346.65			10545.59		
90	11215.29	11239.90		11356.40				
91	11202.36	11221.43		11348.32				
92		11210.65	11355.98	11339.43				
93		11201.04	11344.09	11327.34				
94	11207.18	11190.66	11336.97					
95	11193.84	11177.03	11329.47					
96	11185.22			11327.34				
97	11176.16			11320.97				
98		11172.54		11314.41				
99		11164.62		11307.12				
100		11156.58	11317.54	11297.71				
101		11147.82	11307.12	11281.15				
102	11156.58	11136.92	11298.58					
103	11144.71	11118.46	11291.73					
104	11134.83		11285.29					
105	11126.39		11279.03					
106	11118.46		11272.92					
107	11110.71		11266.74					
108	11103.14		11260.62					
109	11095.53		11254.38					
110	11087.80		11248.03					
111	11080.17		11241.74					
112	11072.37		11234.75					
113	11064.39							
114	11056.26							
115	11047.73							
116								
117								
118								
119								
120								

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Table 2, continued.

V'V''	1.0	0.			1.0	1.0			1.0	2.0		
J	P(J)		R(J)		P(J)		R(J)		P(J)		R(J)	
14					11523.92							
15					11526.50							
16					11524.16		11548.49				10864.45	
17					11521.93		11547.28				10864.13	
18					11519.68		11546.11		10836.86		10863.29	
19					11517.18		11545.01		10834.59		10862.46	
20					11514.75		11544.11		10832.04		10861.66	
21					11512.25		11543.09		10829.37		10860.96	
22					11509.36		A		10827.03		10859.66	
23					11507.03		A		10824.39		10858.47	
24					11504.37		11539.78		10821.68		10857.14	
25					11501.50		11538.41		10818.96		10855.95	
26					11498.62		11536.72		10816.41		10854.45	
27					11495.71			11538.82	10813.53			10856.38
28					11492.17			11537.42	10810.04			10855.01
29						11492.69		11536.08		10810.43		10853.78
30						11489.56		11534.24		10807.51		10852.27
31						11486.43		11532.62		10804.87		10851.09
32						11483.36		11530.77		10801.93		10849.68
33						11480.11		11528.92		10798.85		10847.69
34						11475.78		11526.95		A		10846.20
35						11473.31		11525.82		10792.47		10844.92
36						11469.92		11523.68		A		10843.14
37						11466.30		11520.63		10786.56		10840.90
38			12213.91			11462.78	11524.16	11516.16		10783.18	10844.28	10836.65
39			12210.43			11458.47	11520.47			10779.52	10841.25	
40	12149.50		12207.83		11460.48	11452.63	11518.77		10781.12	10773.24	10839.52	
41	12144.40		12204.83		11455.31		11515.50		10776.72		10836.86	
42	12140.50		12199.38	12207.66	11451.51		11510.42	11520.47	10773.24		10832.17	10840.49
43	12135.95		12189.85	12204.83	11446.86		11500.62	11517.96	10769.02		10823.04	10837.93
44	12129.82	12137.11		12201.88	11440.75	11450.57		11515.50	10762.74	10770.55		10835.39
45	12117.83	12132.68		12198.90	11429.08	11445.83		11512.25	10751.95	10766.84		10833.00
46		12128.02		12195.82		11441.72		11509.95		10762.74		10830.48
47		12123.45		12192.87		11437.61		11507.03		10758.71		10828.30
48		12118.99		12190.15		11433.47		11505.15		10754.64		10825.64
49		12114.29		12186.89		11429.08		11502.01		10750.75		10823.25
50		12109.68		12183.70		11425.38		11499.32		10746.76		10820.79
51		12105.09		12180.62		11420.94		11495.25		10742.76		10818.10
52		12100.39		12177.33		11415.52		11493.10		10738.57		10815.67
53		12095.65		12174.06		11411.96		11490.43		10734.58		10812.87
54		12090.83		12170.63		11407.30		11487.40		10730.33		10810.04
55		12085.88		12166.66		11402.95		11483.98		10726.08		10806.88
56		12080.76	12168.47			11398.36				10721.60		10803.62
57		12075.30	12163.78			11393.43				10716.35		10799.79
58	12075.51		12159.66							10711.32	10801.93	
59	12069.43		12156.06							10706.92	10798.58	
60	12063.77		12151.95						10707.44		A	
61	12058.30		12148.31						10702.73		10792.52	
62	12052.68		12144.40						10698.00		A	
63	12047.49		12140.50						10693.32		10786.20	
64	12042.01		12136.36						10688.58		10783.18	
65	12036.45		12132.12						10683.85		10779.52	
66	12030.77		12127.70						10679.03		10775.84	
67	12024.99		12122.98						10673.99		10771.92	
68	12018.97		12117.83						10669.09		10763.25	
69	12012.67								10663.31		10762.74	
70	12005.99								10658.20			
71									10651.00			

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Table 2, continued.

V'V"	3.0		0.		3.1		1.0		3.0		2.0	
J	P(J)		R(J)		P(J)		R(J)		P(J)		R(J)	
16												
17			13590.88									
18			13590.23									
19	13561.09		13589.54								12213.91	
20	13558.38		13588.72								12212.98	
21	13556.43		13588.04						12181.02		12212.47	
22	13553.61		13586.96						12178.59		12211.66	
23	13551.22		13585.96						12176.43		12210.91	
24	13548.73		13584.91						12174.06		12209.87	
25	13546.32		13583.66				12892.15		12171.60		12209.07	
26	13543.89		13582.42				12891.05		12169.04		12207.66	
27	13540.86		13581.01		12849.44		12889.88		12165.66		12206.96	
28	13538.01		13579.69		12846.84		12888.78		12163.33		12205.28	
29	13534.81		13578.18		12843.64		12887.19		12161.08		12204.59	
30	13531.46		13576.46		12841.05		12885.80		12158.26		12203.33	
31	13528.47		13574.80		12838.10		12884.35		12155.40		12201.88	
32	13525.43		13572.67		12835.04		12882.39		M		12200.08	
33	13522.10		13570.36		12831.68				12149.82		12198.31	
34	13518.18		13567.40	13571.95	12828.34				12146.54		12195.66	12201.20
35	13514.32			13568.48					12142.95			12198.31
36	13509.27	13514.32		13566.25					12138.84	12144.40		12196.37
37		13509.27		13563.86						12139.39		12194.27
38		13505.44		13561.53						12136.36		12192.24
39		13501.28		13558.38						12132.68		12189.85
40		13497.48		13556.43						12126.96		12188.02
41		13493.20	13559.70	13551.22						12124.98		12182.76
42		13489.11	13555.49							12121.27	12187.52	
43	13490.69	13482.32	13553.04							12114.29	12185.31	
44	13484.98		13550.03						12118.27		12193.53	
45	13490.74		13547.16						12114.29		12181.02	
46	13476.28		13543.89						12110.91		12178.59	
47	13471.63		13540.86						12106.80		12176.09	
48	13466.78		13537.21						12102.76		12170.63	
49	13462.12		13532.23	13540.86					12098.90		12169.04	12177.38
50	13456.98			13535.14					12094.48			12172.16
51	13450.53	13459.08		13531.46					12087.85	12097.07		12169.68
52		13452.03		13527.88				12843.30		12090.04		12166.12
53		13446.58		13524.66				12840.10		12085.88		12163.78
54		13441.29		13520.93		12757.25		12836.99		12081.30		12161.00
55		13436.42		13518.18		12752.53		12833.76		12077.00		12158.26
56		13431.46		13514.57		12747.91		12830.57		12072.64		12155.34
57		13426.95		13510.99		12743.13		12827.39		12068.21		M
58		13421.85		13507.27		12738.44		12824.06		12063.77		12149.34
59		13416.50		13503.33		12733.50		12820.67		12059.37		12146.54
60		13411.23		13500.04		12728.74		12817.45		12054.84		M
61		13406.09		13495.88		12723.83		12813.80		12050.31		12140.08
62		13400.68		13492.11		12713.83		12810.47		12045.63		12137.11
63		13395.20		13488.30		12713.76		12806.85		12041.02		12133.88
64		13387.80		13484.26		12708.70		12802.98		12036.45		12130.62
65		13384.19		13479.93		12703.57		12799.37		12031.57		12127.70
66		13378.62				12698.31		12795.47		12026.76		12123.79
67		13372.98				12693.04		12791.67		12021.84		12120.33
68						12687.63		12786.96		12016.60		12115.99
69						12682.20				12011.84		12111.31
70						12675.96				12005.99		12105.09
71										11998.67		
72										11992.03		

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Table 2, continued.

V'V"	4.0	1.0			4.0	2.0		
J	P(J)		R(J)		P(J)		R(J)	
15	13551.86		13574.80					
16	13550.03		13574.34					
17	13547.97		13573.91					
18	13545.99		13573.29					
19	13543.89		13572.67					
20	13541.66		13571.95					
21	13539.58		13571.16					
22	13537.21		13570.36					
23	13534.81		13569.50					
24	13532.23		13568.48		12849.45			
25	13529.91		13567.40		12847.29		12884.59	
26	13527.19		13566.25		12844.76		12883.85	
27	13524.66		13565.05		12842.25		12882.81	
28	13522.10		13563.86		12839.63		12881.56	
29	13519.05		13562.47		12836.99		12880.43	
30	13516.18		13561.09		12834.41		12879.20	
31	13513.37		13559.70		12831.72		12877.87	
32	13510.30		13558.22		12828.84		12876.63	
33	13507.27		13556.43		12825.97		12875.14	
34	13503.93		13554.75		12822.86		12873.78	
35	13500.66		13553.04		12819.96		12872.41	
36	13497.48		13551.22		12816.83		12870.31	
37	13494.18		13549.22		12813.80		12868.66	
38	13490.65		13547.16		12810.47		12867.14	
39	13487.26		13545.25		12807.09		A	
40	13483.61		13543.25		12803.94		A	
41	13479.93		13540.36		12800.59		A	
42	13476.28		13538.76		12797.04		A	
43	13472.53		13536.32		12793.57		A	
44	13468.67		13533.00	13540.86	12789.92		12854.33	
45	13464.70		13226.97	13533.00	12786.29		12848.56	
46	13459.72	13467.62		13529.01	12781.49			12850.86
47	13452.03	13458.29		13526.49	12774.71			12848.56
48		13452.67		13523.76		12775.07		12846.12
49		13448.36		13520.93		12771.14		12843.64
50		13444.21		13518.18		12767.13		12841.05
51		13439.84		13515.19		12763.17		12838.58
52		13435.52	13514.57	13508.43		12759.05	12838.11	12831.61
53		13430.97	13509.27			12754.92	12833.40	
54	13428.58	13422.60	13506.15		12752.90	12746.49	12830.36	
55	13421.85		13503.01		12746.49		12827.45	
56	13417.13		13500.04		12742.04		12825.07	
57	13412.47		13496.55		12737.72		12821.79	
58	13407.87		13493.20		12733.50		12818.80	
59	13402.34		13489.62		12728.79		12814.99	
60	13397.87		13484.54		12724.05		12810.49	
61	13392.87		13477.65	13484.26	12718.83		12803.94	12811.56
62	13386.03			13478.98	12712.68			12806.05
63	13377.63	13384.19		13475.15	12704.65	12712.01		12802.93
64		13377.63		13471.63		12705.57		12799.37
65		13372.32		13467.98		12700.63		12796.15
66		13367.01		13463.84		12695.44		12792.46
67		13361.60		13459.72		12690.66		12789.05
68		13356.01		13455.77		12685.36		12784.81
69		13350.14		13452.03		12680.61		12782.58
70		13344.81				12675.58		
71		13339.45				12670.68		
72								

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Table 2., continued

J	5.0 2.0 P(J)		R(J)		5.0 3.0 P(J)		R(J)		6.0 3.0 P(J)		R(J)	
25											13547.16	
26											13546.32	
27									13504.88		13545.25	
28									13502.49		13543.89	
29									13500.04		13543.25	
30									13497.48		13542.27	
31			13547.97				12875.14		13494.86		13540.86	
32			13546.32				12873.78		13492.11		13539.58	
33	13495.88		13544.86		12823.36		12872.41		13489.11		13533.01	
34	13492.86		13543.25		12820.60		12871.44		13486.24		13536.32	
35	13489.62		13541.66		12817.41		12869.61		13483.12		13534.09	
36	13486.41		13539.58		12814.60		12867.86		13479.93		13533.00	
37	13483.12		13538.01		12811.54		12866.31		13476.28		13531.46	
38	13479.93		13536.32		12808.51		A		13473.52		13529.91	
39	13476.28		13534.09		12805.19		A		13470.16		13527.88	
40	13472.86		13532.10		12801.86		A		13467.25		13525.43	
41	13469.41		13529.91		12798.59		A		13463.84		13523.26	13540.86
42	13465.80		13527.88		12795.43		A		13459.72		13520.93	13532.23
43	13462.12		13525.62		12792.01		12855.35		13455.77	13473.52		13526.91
44	13458.29		13523.26		12788.45		12853.13		13452.03	13463.31		13524.66
45	13454.44		13520.93		12784.78		12851.15			13456.40		13522.56
46	13450.53		13518.18		12780.92		12848.56			13452.67		13520.38
47	13446.58		13514.32		12777.40		12844.78			13449.04		13518.18
48	13442.22			13515.89	12773.60		12840.23	12846.84		13445.24		13515.89
49	13436.92			13512.24	12768.21			12843.64		13441.29		13513.37
50		13436.92		13509.27	12761.88	12768.64		12841.01		13437.51		13510.99
51		13431.46		13506.15		12763.65		12838.53		13433.53		13508.43
52		13426.95		13503.33		12759.39		12835.95		13429.37		13505.44
53		13422.60		13500.68		12755.29		12833.37		13425.46	13512.73	13501.23
54		13418.11		13497.48		12751.09		12830.54		13420.86	13506.15	13494.18
55		13413.61		13494.45		12746.97		M	13426.61	13415.25	13501.91	
56		13409.19		13491.48		12742.90		12825.03	13418.57	13408.28	13499.14	
57		13404.50		13488.30		12738.44		12822.64	13412.62		13495.88	
58		13399.79		13484.98		12734.27		M	13408.28		13492.86	
59		13395.20		13481.68		12730.25		12816.85	13403.66		13488.30	
60		13390.39		13478.51		12725.83		12813.76	13399.14			
61		13385.54		13475.15		12721.52		12811.01	13392.87			
62		13380.72		13471.63		12717.47		12808.51				
63		13375.75		13467.98		12712.68		12805.00				
64		13370.72		13464.30		12708.18		12801.93				
65		13365.67		13460.82		12703.57		12798.62				
66		13360.52		13456.98		12698.83		12795.47				
67		13355.31		13453.40		12694.41		12792.46				
68		13350.14		13449.45		12689.42		12789.05				
69		13344.81		13445.60		12684.82		M				
70		13339.46		13441.76		12679.97		12782.59				
71		13334.08				12674.94						
72		13328.56				12670.15						
73												

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Table 2, continued.

V'V" / J	2.0 0. P(J)		R(J)		2.0 1.0 P(J)		R(J)		2.0 3.0 P(J)		R(J)	
3												
4	12909.52											
5	12908.32											
6	12907.21											
7	12906.76											
8	12904.54											
9	12903.10											
10	12901.63						12223.81					
11	H						12223.61					
12	12898.24				12205.28		12223.81					
13	12896.51				12203.63		12223.57					
14	12894.93		12915.36		12201.38		12223.30					
15	12893.07		12915.93		12200.08		12223.04					
16	12891.00		12915.46		12198.31		12222.75					
17	12889.02		12914.91		12196.37		12222.27					
18	12886.80		12914.31		12194.27		12221.82		10836.65		10864.13	
19	12884.59		12913.60		12192.24		12221.15		10834.59		10863.62	
20	12882.39		12912.35		12190.15		12220.56		10832.54		10862.95	
21	12879.96		12912.04		12188.02		12219.99		10830.48		10862.46	
22	12877.79		12911.08		12185.72		12219.01		10828.30		10861.06	
23	12875.14		12910.11		12183.53		12218.13		10826.33		10860.96	
24	12872.88		12909.05		12181.02		12217.24		10824.23		10860.39	
25	12870.33		12907.99		12178.59		12216.28		10822.05		10859.66	
26	A		12906.74		12176.09		12214.95		10819.74		10858.95	
27	A		12905.51		12173.46		12213.91		10817.48		10858.16	
28	A		12904.15		12170.63		12212.98		10815.17		-D.	
29	A		12902.72		12167.96		12211.65		10812.87		10856.38	
30	12856.25		12901.25		12165.35		12210.43		10810.43		10855.50	
31	12853.15		12899.79		12162.46		12209.07		10807.49		10854.45	
32	12850.01		12897.99		12159.56		12207.66		10805.43		10853.38	
33	12846.34		12896.50		12156.57		12206.25		10802.81		10852.27	
34	12843.60		12894.63		12153.53		12204.59		10800.17		10851.09	
35	12840.26		12892.85		12150.46		12202.90		10797.42		10849.89	
36	12836.99		12890.60		12147.31		12201.20		A		10848.62	
37	12833.76		12888.75		12144.00		12199.33		10791.95		10847.26	
38	12829.94		12885.79		12140.50		12197.54		A		10845.67	
39	12826.25		12884.52		12137.32		12195.66		10786.20		10844.28	
40	12822.64		12882.40		12133.88		12193.60		10783.18		10842.82	
41	12818.83		12879.95		12130.33		12191.41		10780.02		10840.90	
42	12814.95		12876.67		12126.74		12186.55		10776.97		10838.97	
43	12811.01		12872.81		12122.98		12184.59	12201.88	10773.24		10835.21	10852.04
44	12806.95		12860.29		12118.39		12173.59	12192.87	10770.02		10830.14	10843.14
45	12800.58				12113.17	12130.35		12186.89	10764.42	10781.42		10837.83
46	12792.46				12105.37	12119.59		12183.70	10758.47	10770.98		10835.21
47						12112.08		12181.02		10764.10		10833.00
48						12107.28		12178.00		10760.03		10830.89
49						12103.01	12184.27	12174.57		10756.19	10838.60	10828.61
50						12098.45	12178.00	12169.68		10752.62	10832.54	
51					12103.23	12093.55	12173.48	12173.00	10758.71	10748.70	10829.00	10834.59
52					12095.38	12086.97	12169.68	12173.19	10751.19		10825.64	10830.46
53					12089.27	12093.71	12165.55	12169.68	10745.94	10751.79	10822.05	10827.77
54					12083.76	12087.39		12166.66	10741.91	10745.94		10825.18
55				12348.57	12078.19	12082.28		12163.33	10736.03	10741.91		10823.04
56				12344.76		12077.52		12160.30		10737.65		10820.79
57		12757.25		12341.09		12072.64		12157.05		10733.86		10818.10
58		12752.01		12337.01		12068.21		12153.53		10730.18		10815.17
59		12746.49		12333.08		12063.09		12149.82		10726.08		10812.87
60		12741.05		12328.32		12057.95		12145.16		10721.60		10808.69
61		12735.39	12827.39			12052.68	12145.65			10717.11	10809.70	

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Table 2, continued.

V'V"	2.0 0.				2.0 1.0				2.0 3.0			
J	P(J)		R(J)		P(J)		R(J)		P(J)		R(J)	
62		12729.27	12821.68			12046.88	12140.62			10711.82	10805.43	
63	12726.42		12816.33		12045.62		12136.36		10711.22		10801.93	
64	12719.44		12810.47	12823.36	12039.16		12129.82	12141.75	10705.50		10796.38	10809.70
65	12712.68		12799.75	12816.85	12033.30		12120.33	12135.95	10700.42		10787.64	10804.87
66	12705.23	12717.72		12811.54	12024.99	12037.10		12131.23	10693.32	10706.65		10800.59
67	12692.65	12709.76		12806.05	12014.05	12029.68		12126.18	10683.10	10700.42		A
68		12702.79		12799.37		12023.24		12120.33		10694.43		10791.13
69		12695.36	12809.18			12016.60	12131.23	12113.17		10688.58		10785.45
70		12687.03	12799.75			12009.43	12120.33	12106.04		10681.95		10779.72
71	12695.86		12792.42		12018.47	12001.47	12113.66	12093.71		10674.82		
72	12684.32		12786.30		12006.43	11992.03	12108.24			10666.51		
73	12675.96		12780.92		11998.02	11978.15	12103.23					
74	12668.23		12775.50		11991.04		12098.45					
75	12661.16		12770.37		11984.51		12093.71					
76	12654.28		12765.22		11978.15		12089.07					
77	12647.67		12760.24		11971.91		12084.48					
78	12641.02		12755.32		11965.74		12079.82					
79	12634.34		12750.00		11959.57		12074.98					
80	12628.03		12744.75		11953.31		12070.43					
81	12621.00		12739.42		11947.22		12065.65					
82	12614.29		12734.27		11940.97		12060.84					
83	12607.44		12728.74		11934.68		12055.92					
84	12600.36		12723.16		11928.36		12050.80					
85	12593.62		12717.72		11921.74		12045.63					
86	12586.45		12711.41		11915.22		12040.27					
87	12579.72		12705.53		11908.48		12034.36					
88	12571.84				11901.36		12028.33	12044.81				
89	12564.38				11894.25			12036.05				
90					11886.78	11903.04		12029.68				
91						11892.86		12023.24				
92						11884.92		12016.81				
93						11877.25		12011.27				
94						11869.64						
95						11862.10						
96												
97												
98												
99												

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Table 3. Rotational Contants for the X'Σ and A'Σ States: CaO^{18}

v	B"obs.	B"calc.	B'obs.	B'calc'.
0	.3732	.3728	.4078	.4078
1	.3725	.3720	.4049	.4048
2	.3706	.3710	.4017	.4018
3	.3698	.3702	.3988	.3988
4	.3693	.3692		
5	.3681	.3684		
6	.3678	.3674		

Table 4. Spectroscopic Constants: CaO^{18}

	Constants for $X^1\Sigma$		Constants for $A^1\Sigma$	
	found	Cal from CaO^{16}	found	Cal from CaO^{16}
v(0,0)	0.0	0.0	11548.6	11548.80
ωe	702.18	702.40	~686.5	686.9
ωexe	4.29	4.43	~1.5	1.47
Be	.4093	.4091	.3733	.3740
αe	.003	.00296	.0009	.0012
De	$\sim 5.24\times10^{-7}$	5.56×10^{-7}	$< 4.58\times10^{-7} >$	4.57×10^{-7}
βe	$\sim 5.9\times10^{-8}$	2.4×10^{-8}		

Table 5. Summary of the Perturbations: CaO^{18}

V_P	$V_{A^1\Sigma}$	J_o	B_v^P	B_v^P (Slope)
Z	0	38.70	.304	
Q	0	48.50		
Y	0	56.20	.3088	
W	0	63.20	.328	
X	0	67.80		
Z + 1	0	87.80	.3018	
Q + 1	0	89.90	.2938	
Y + 1	0	93.50	.306	.284
W + 1	0	96.50		.281
X + 1	0	101.10	.311	
Z + 2	0	~114.00		.280
Y + 1	1	27.00		.284
W + 1	1	38.80		.281
X + 1	1	42.40	(.295)	
B	1	57.90	(.35)	
Z + 2	1	~70.70		.280
Z + 3	2	44.80	.269	
B + 1	2	53.	.35	
Q + 3	2	51.40		
Y + 3	2	61.40		
W + 3	2	64.90	.314	
X + 3	2	71.00	.3025	
Z + 4	2	~89.75		
Y + 4	3	35.00		
W + 4	3	42.00		
X + 4	3	50.00		

Table 5. Summary of the Perturbations: CaO^{18} (continued)

V_P	$V_{A^1\Sigma}$	J_o	B_v^P	B_v^P (Slope)
Z + 5 Z + 6	3 4	~70.60 45.70		
Q + 6 Y + 6 (?)	4 4	52.70 61.70		
X + 6 Y + 7 (?)	4 5	~70.50 ~31.50		
X + 7 Z + 8	5 5	48.50 ~71.75		
Z + 9 Y	6 6	43.10 54.60	 .3012	
	6	~60.60		

Table 6. Term Values of the Perturbing States at J=0 for CaO^{18}

Z	12010	Q	12100	Y	12170	W	12270	X	12300
Z + 1	12480	Q + 1	12565	Y + 1	12650	W + 1	12720	X + 1	12730
Z + 2	12945	Q + 2	13035	Y + 2	13120	W + 2	(13190)	X + 2	(13210)
Z + 3	13405	Q + 3	13485	Y + 3	13595	W + 3	13645	X + 3	13705
Z + 4	(13880)	Q + 4	13940	Y + 4	14060	W + 4	14105	X + 4	14160
Z + 5	14300							X + 5	(14605)
Z + 6	14755			Y + 6 (?)	14940			X + 6	15010
Z + 7	(15200)	B	12650	Y + 7 (?)	15370			X + 6	15480
Z + 8	15640	B + 1	13322	Y + 8 (?)	16235				
Z + 9	16070								

Table 6, continued. Term Values of the Perturbing States at J=0 for CaO^{16}

Z	12165	Q	12735	Y	12325	X	12430
Z + 1	12660	Q + 1	13235	Y + 1	12820	X + 1	12885
Z + 2	13155	Q + 2	13710	Y + 2	(13295)	X + 2	13345
Z + 3	13680	Q + 3	14210	Y + 3	13780	X + 3	13850
Z + 4	14155			Y + 4	14250	X + 4	14340
Z + 5	(14590)					X + 5	14800
Z + 6	15125	B	12113			X + 6	(15280)
Z + 7	15635	B + 1	12690			X + 7	15765
						X + 8	16220

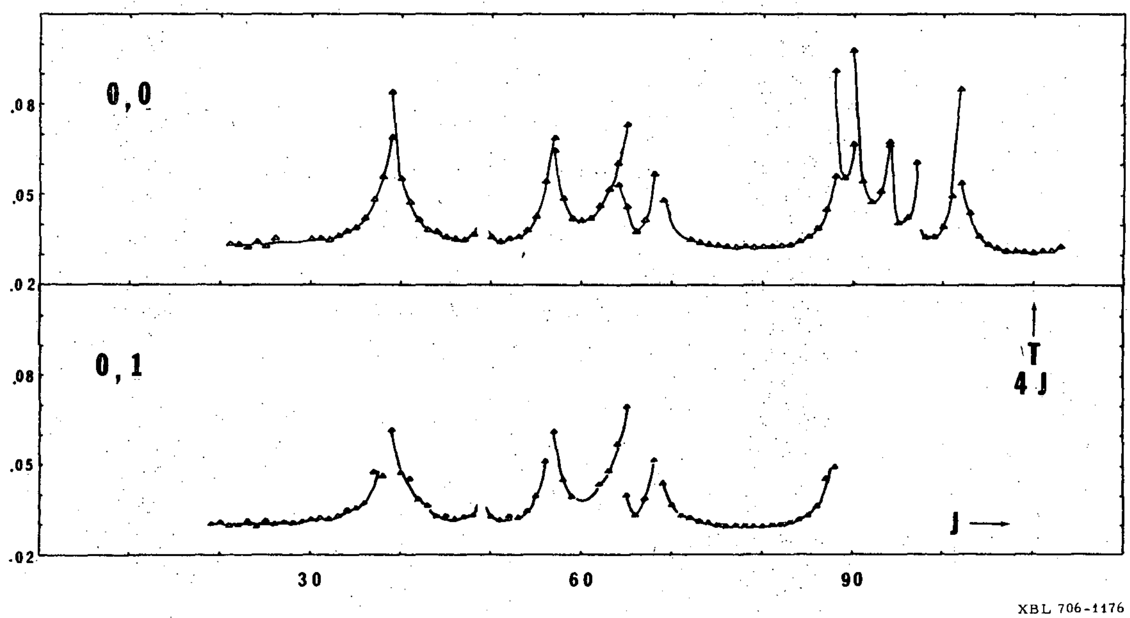

Fig. 8. T/4J = [R(J-2) - R(J-1) + P(J) - P(J+1)]/4J plotted vs J for the (0,0) and)0,1) bands.

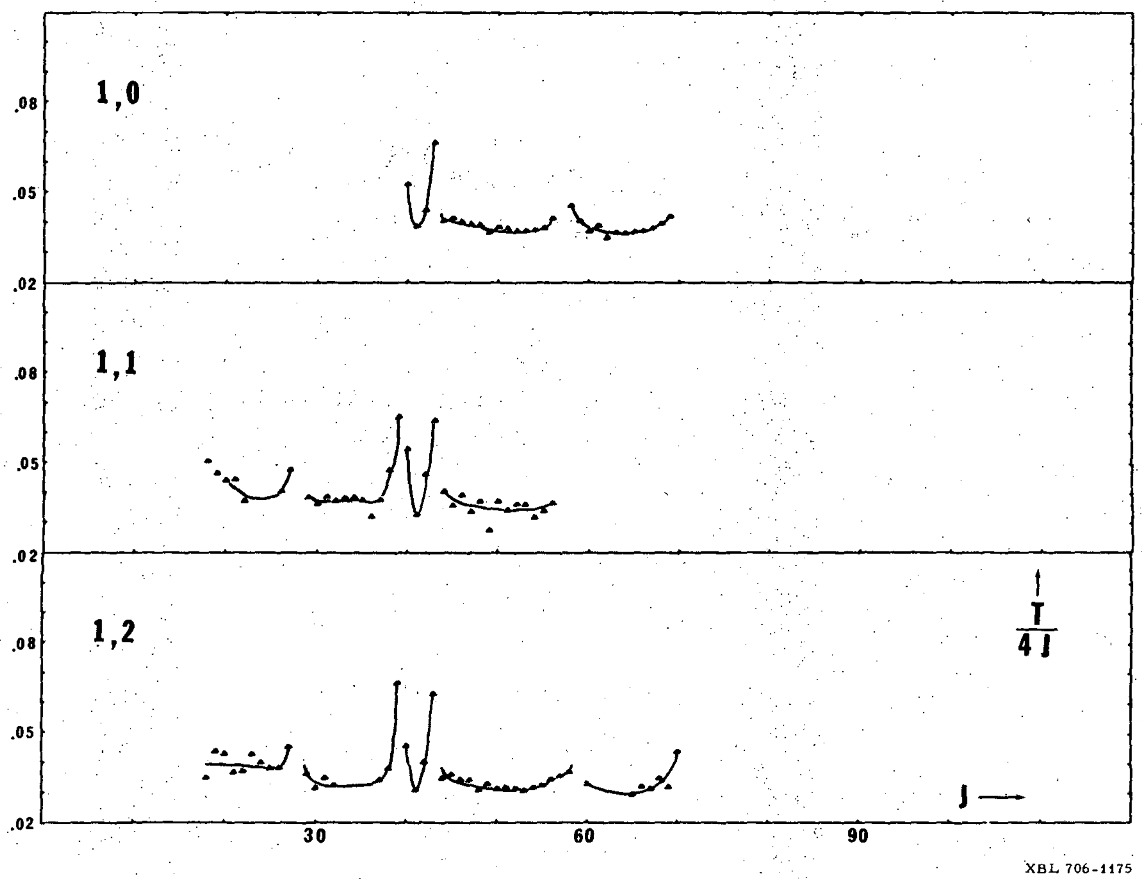

Fig. 9. T/4J plotted against J for the (1,0), (1,1), and (1,2) bands.

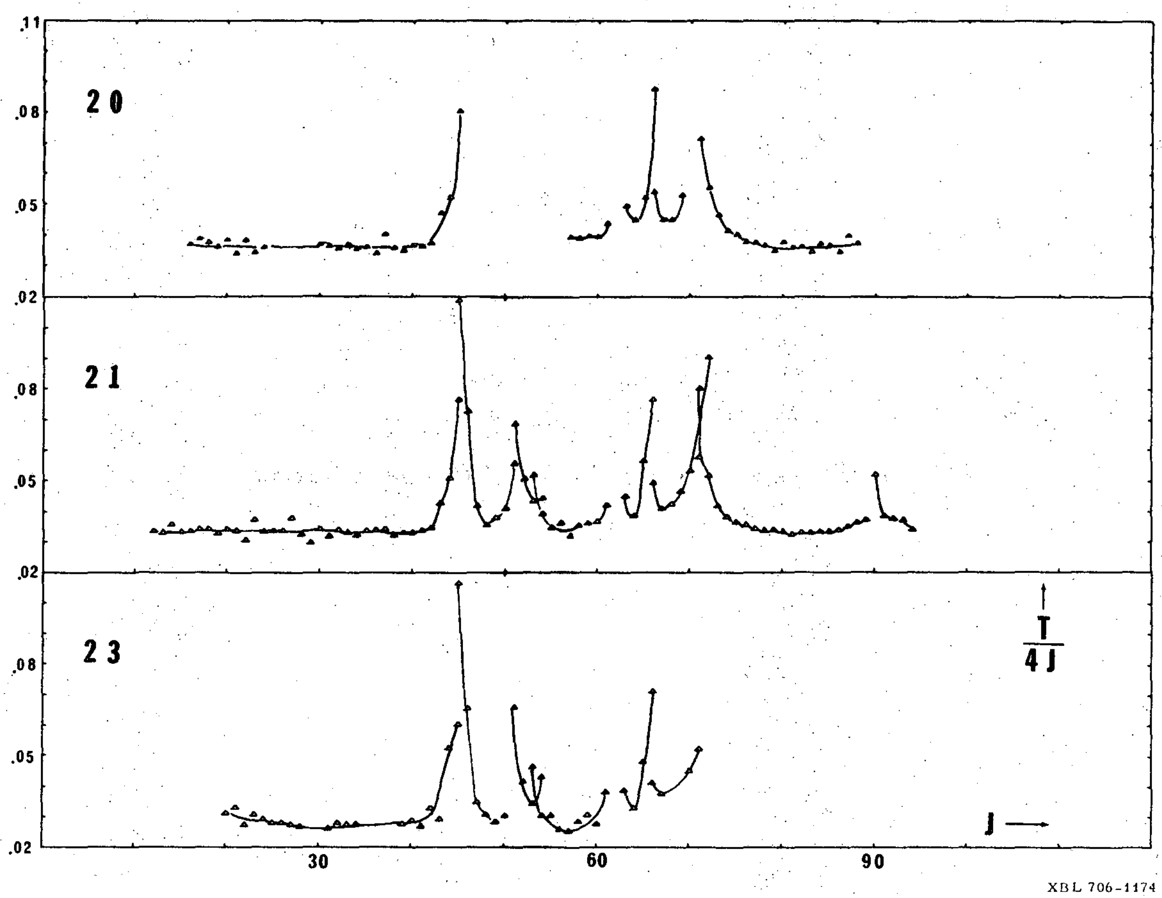

Fig. 10. T/4J plotted against J for the (2,0), (2,1), and (2,3) bands. The blank spot in the (2,0) plot is due to atomic lines which blotted out the CaO spectra.

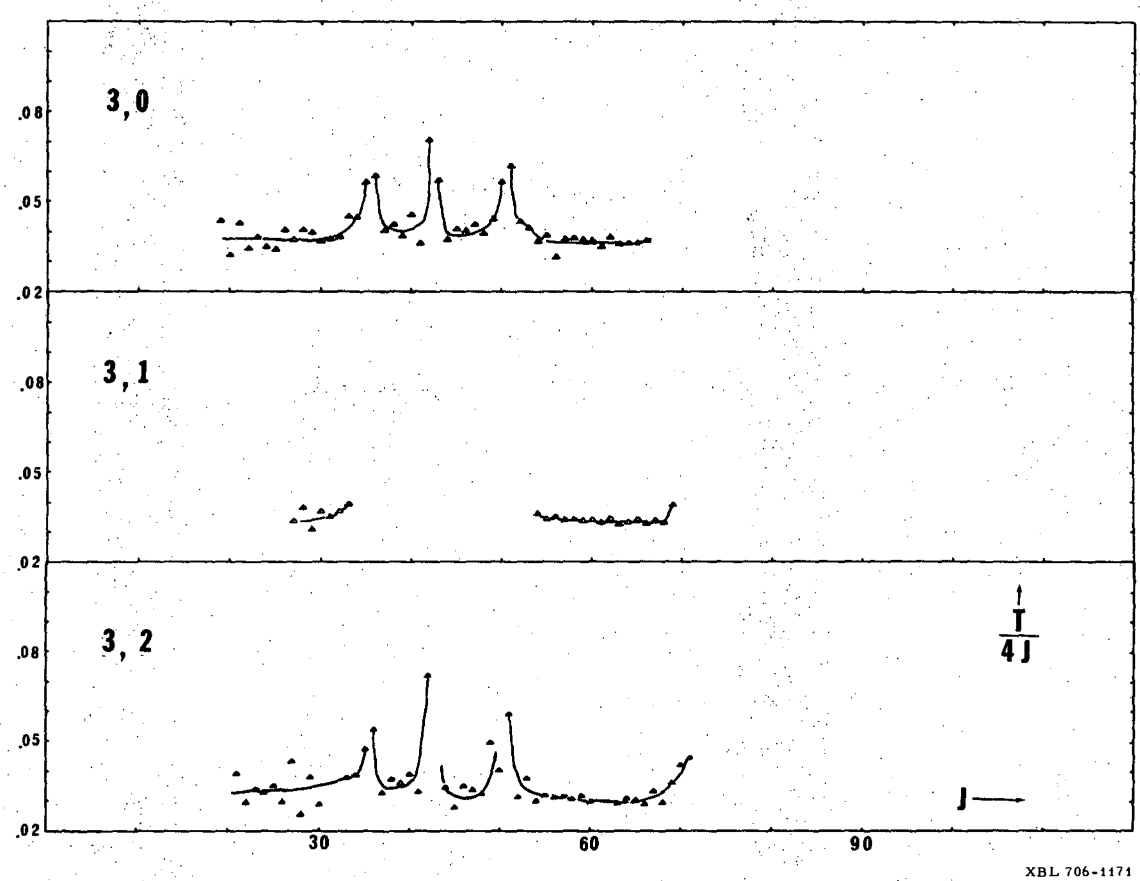

Fig. 11. T/4J plotted vs J for the (3,0), (3,1), and (3,2) bands.

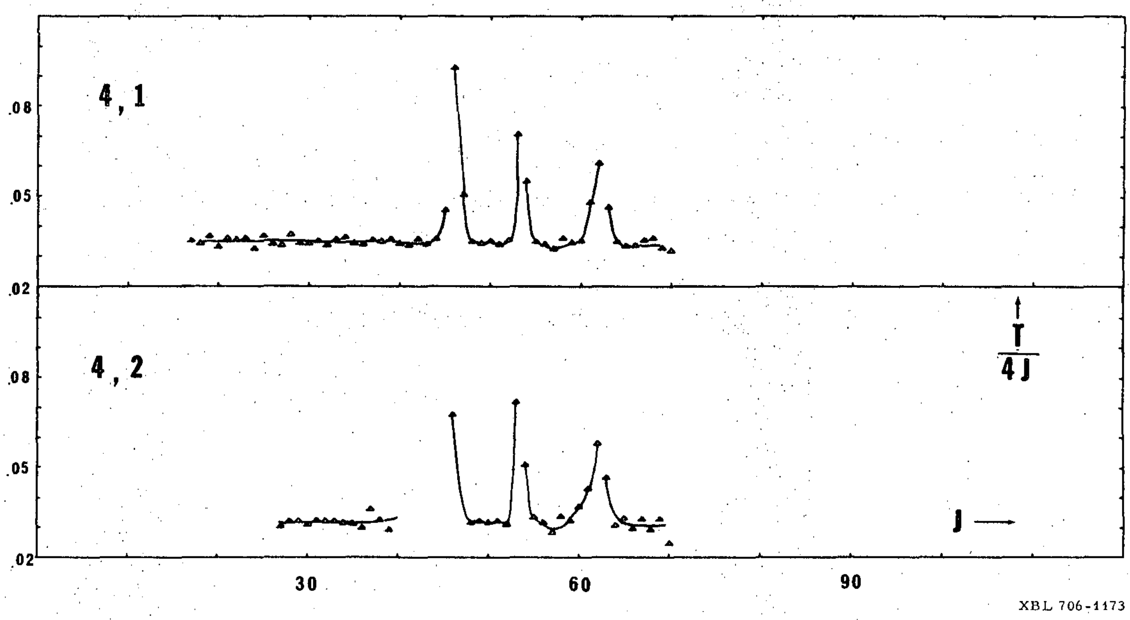

Fig. 12. T/4J plotted against J for the (4,1) and (4,2) bands.

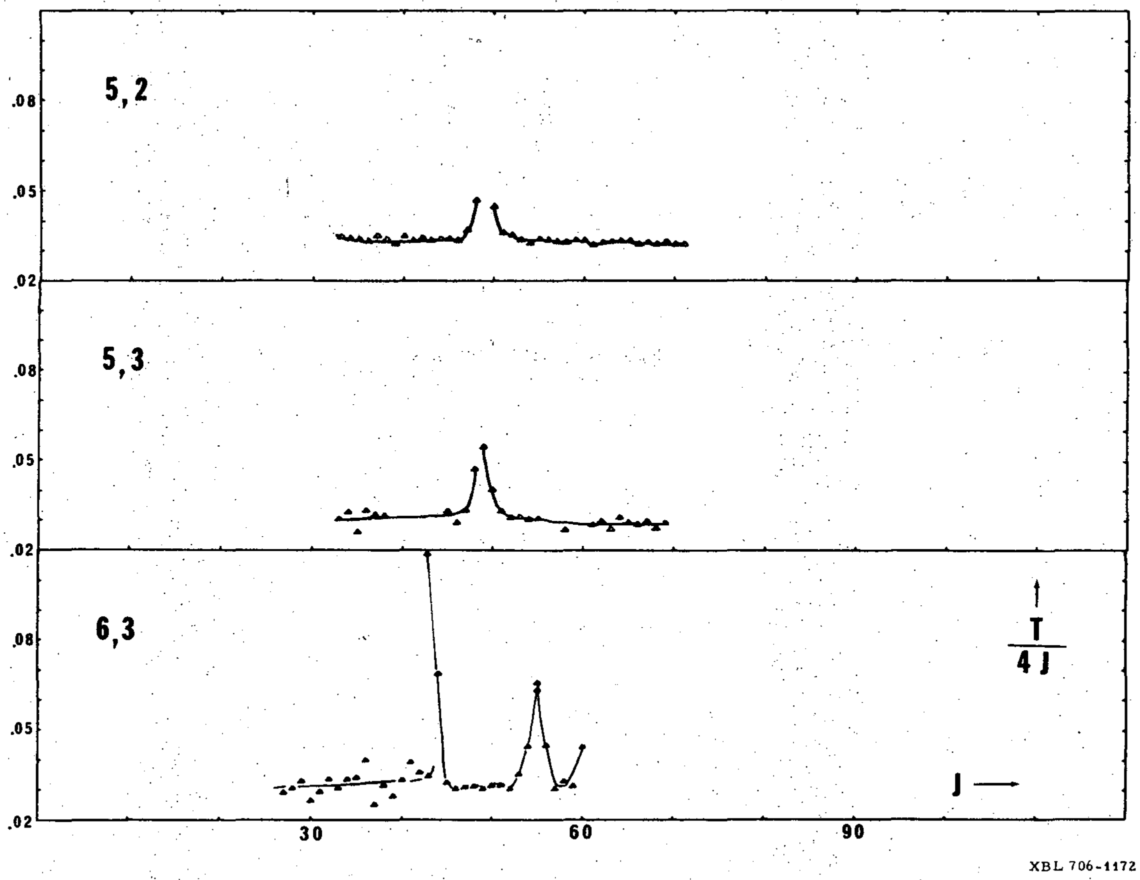

Fig. 13. T/4J plotted against J for the (5,2), (5,3), and (6,3) bands.

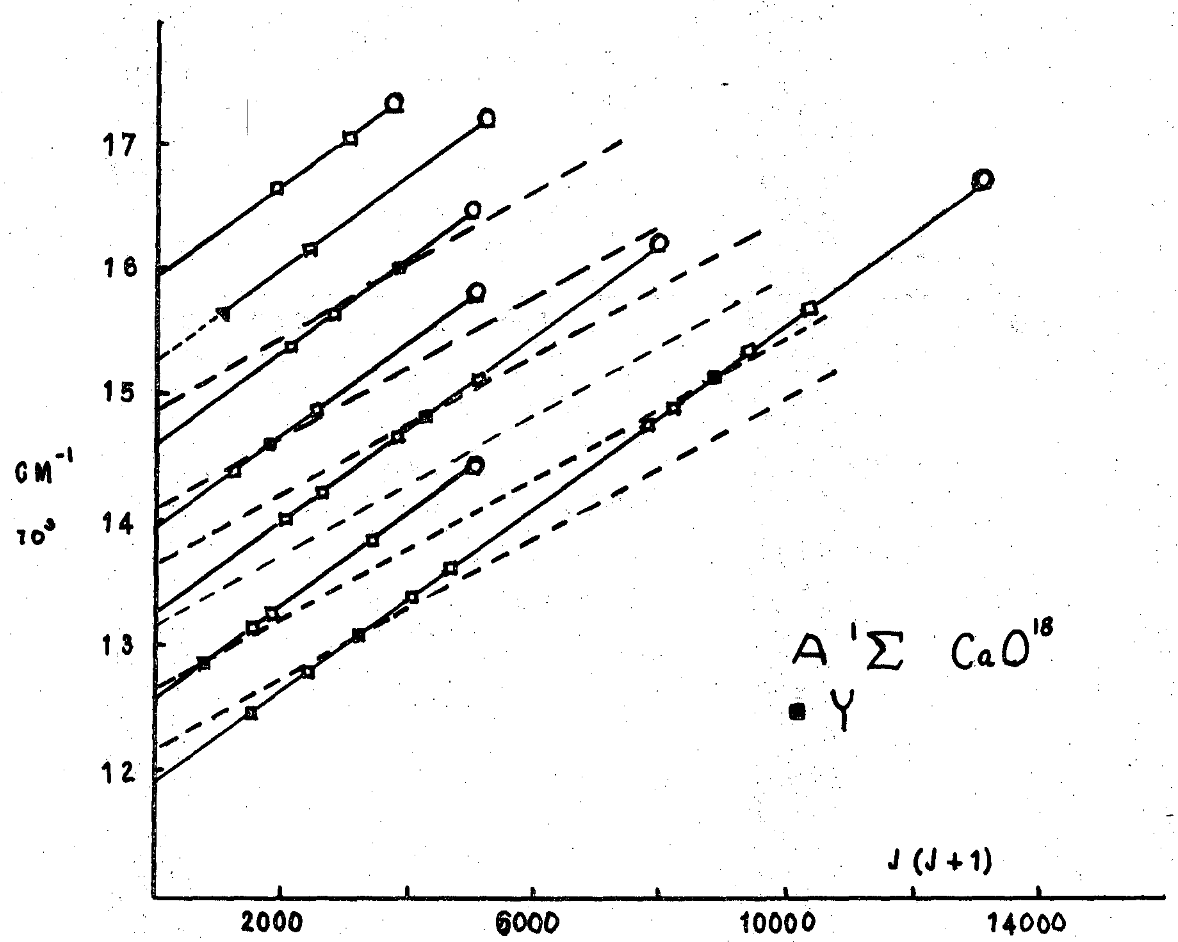

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Fig. 14. Plot of energy vs J(J+1). The solid lines represent the first seven vibrational levels of the A'Σ state of CaO^{18} and the squares show the positions of the perturbations. The dashed lines indicate some vibrational levels of the Y^{18} perturbing state.

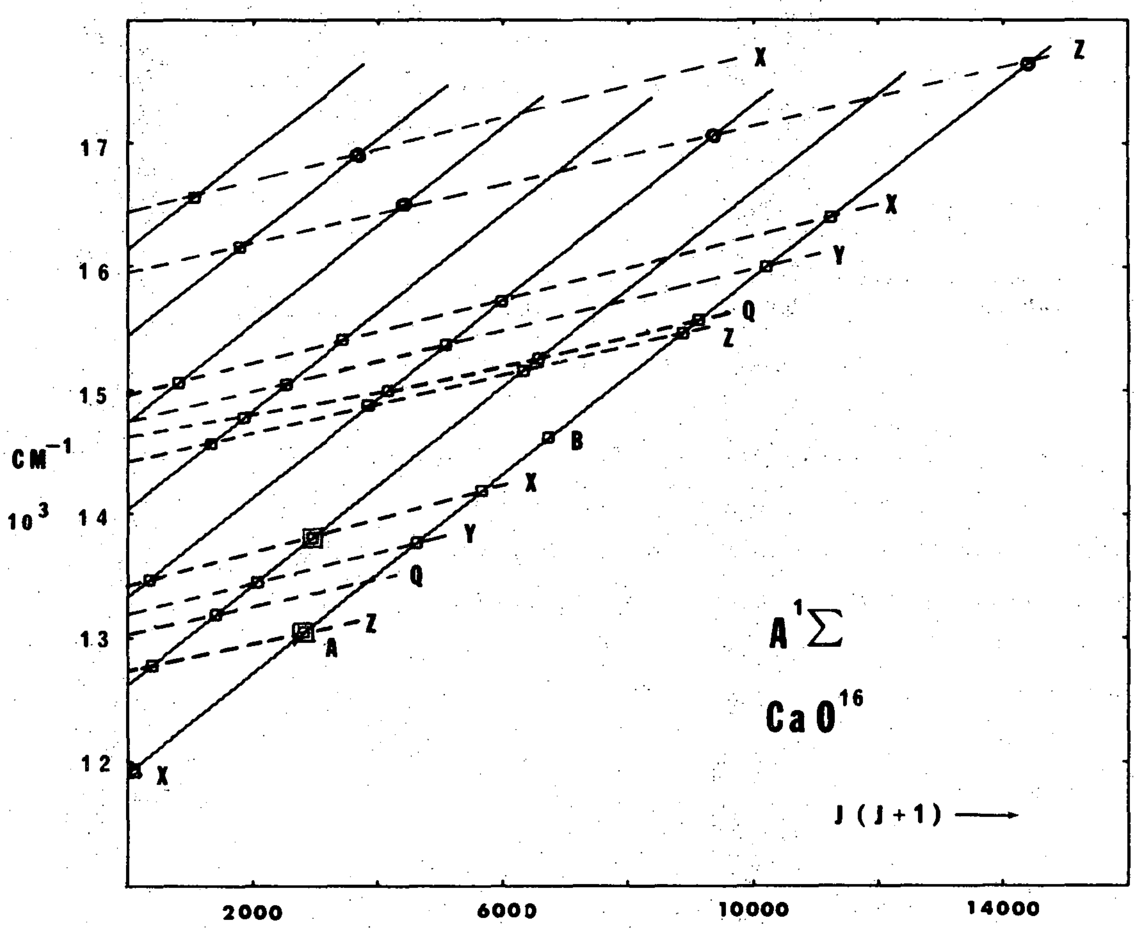

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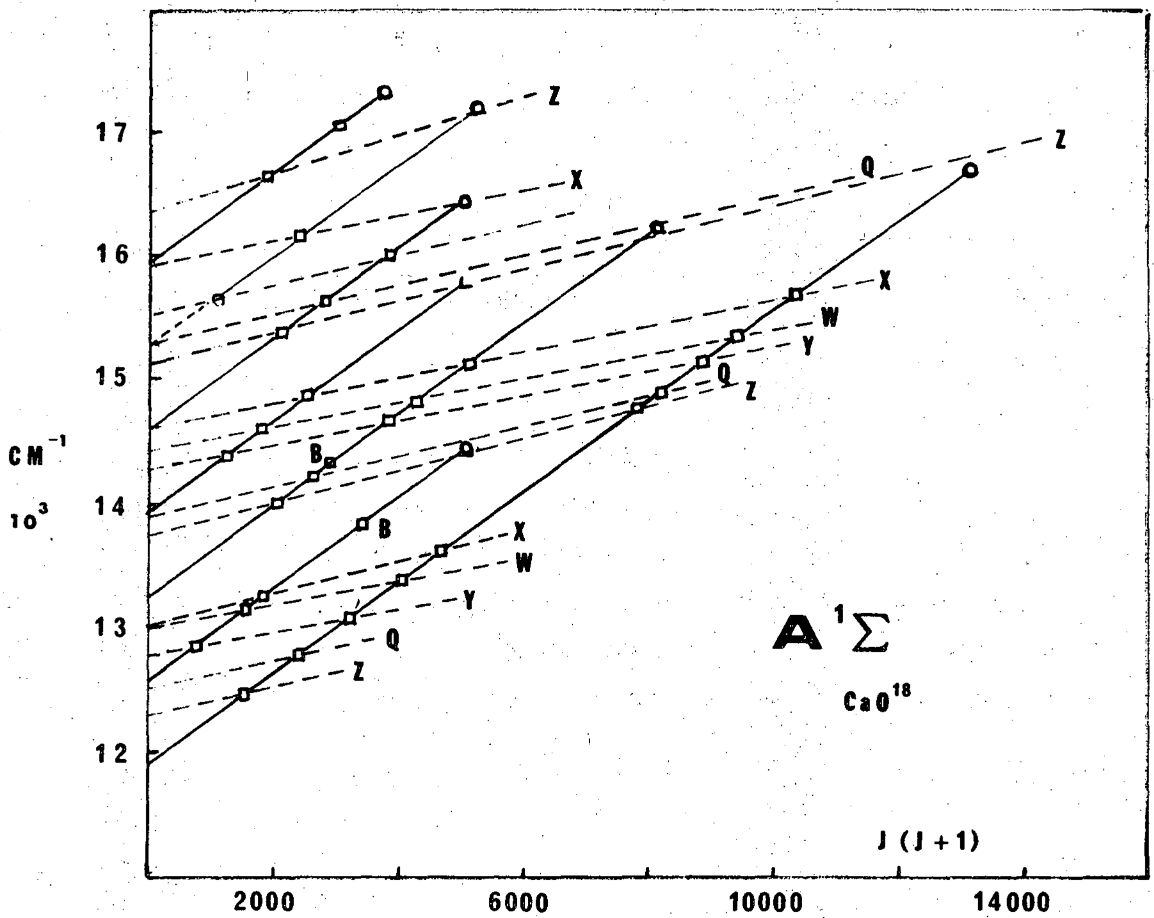
Fig. 15. Plot of energy vs J(J+1). The solid lines represent the vibrational levels of the A'Σ state of CaO^{16}, the squares indicate perturbations, and the dashed lines connect perturbations arising from the same perturbing state. The zero of energy has been taken as the bottom of the X'Σ potential curve.



XBL 706-1167

Fig. 16. Plot of energy vs J(J+1). The solid lines show the vibrational levels of the A'Σ state of CaO^{18}, the squares indicate perturbations, and the dashed lines connect perturbations arising from the same perturbing state. The circles indicate the end of the analysis. The zero of energy is the bottom of the X'Σ potential curve.

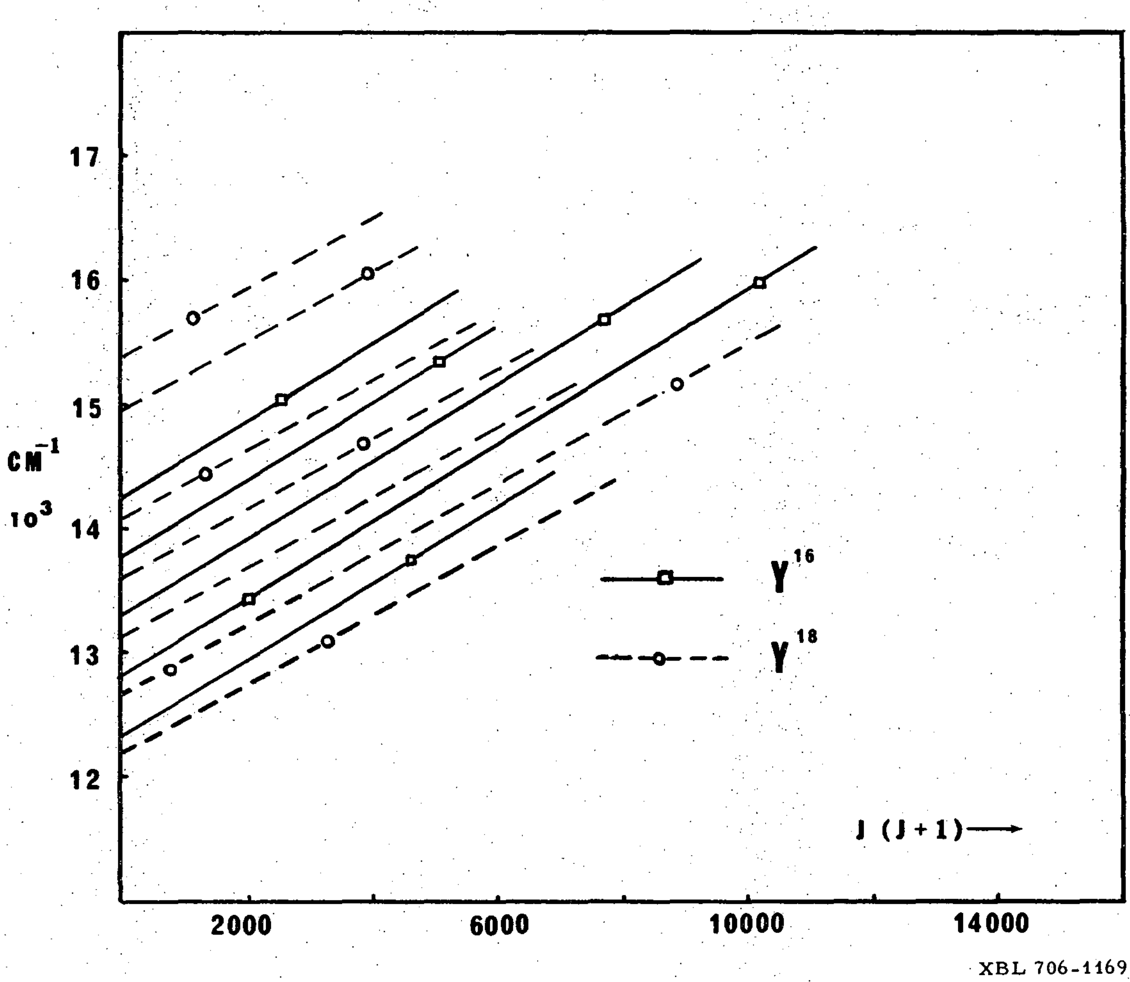


Fig. 17. Plot of energy vs J(J+1) showing the vibrational levels of the Y^{16} and Y^{18} perturbing states.

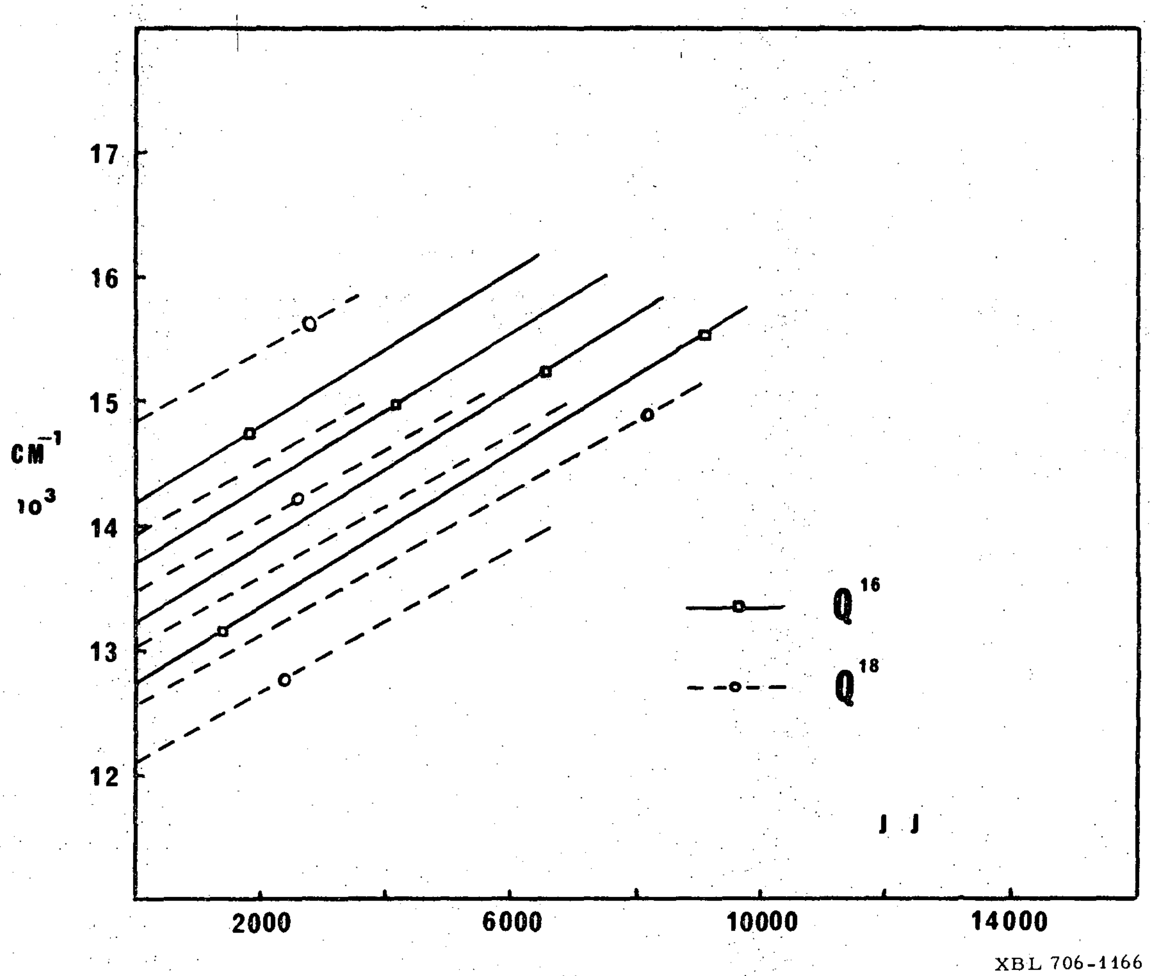


Fig. 18. Plot of energy vs J(J+1) showing the vibrational levels of the Q^{16} and Q^{18} perturbing states.

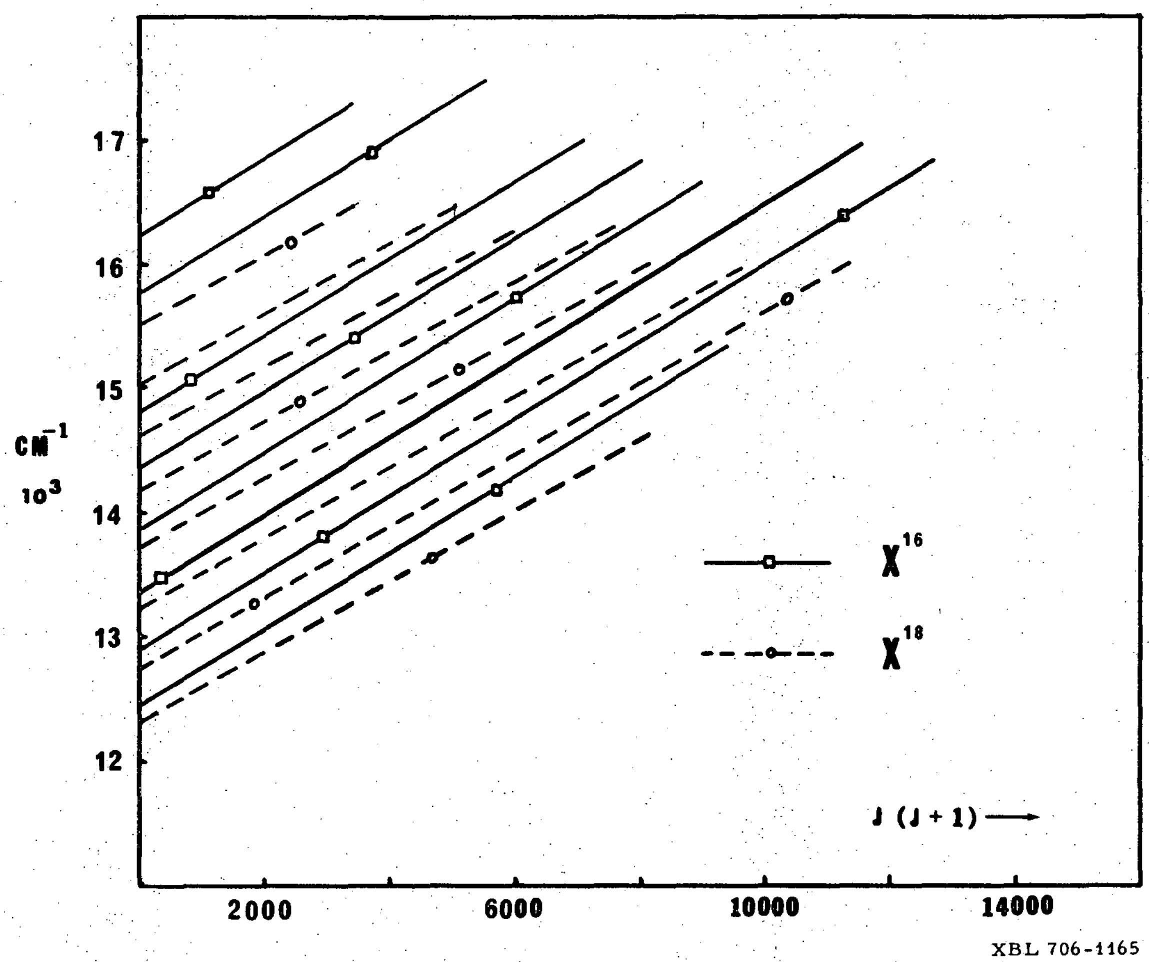


Fig. 19. Plot of energy vs J(J+1) showing the vibrational levels of the X^{16} and X^{18} perturbing states.

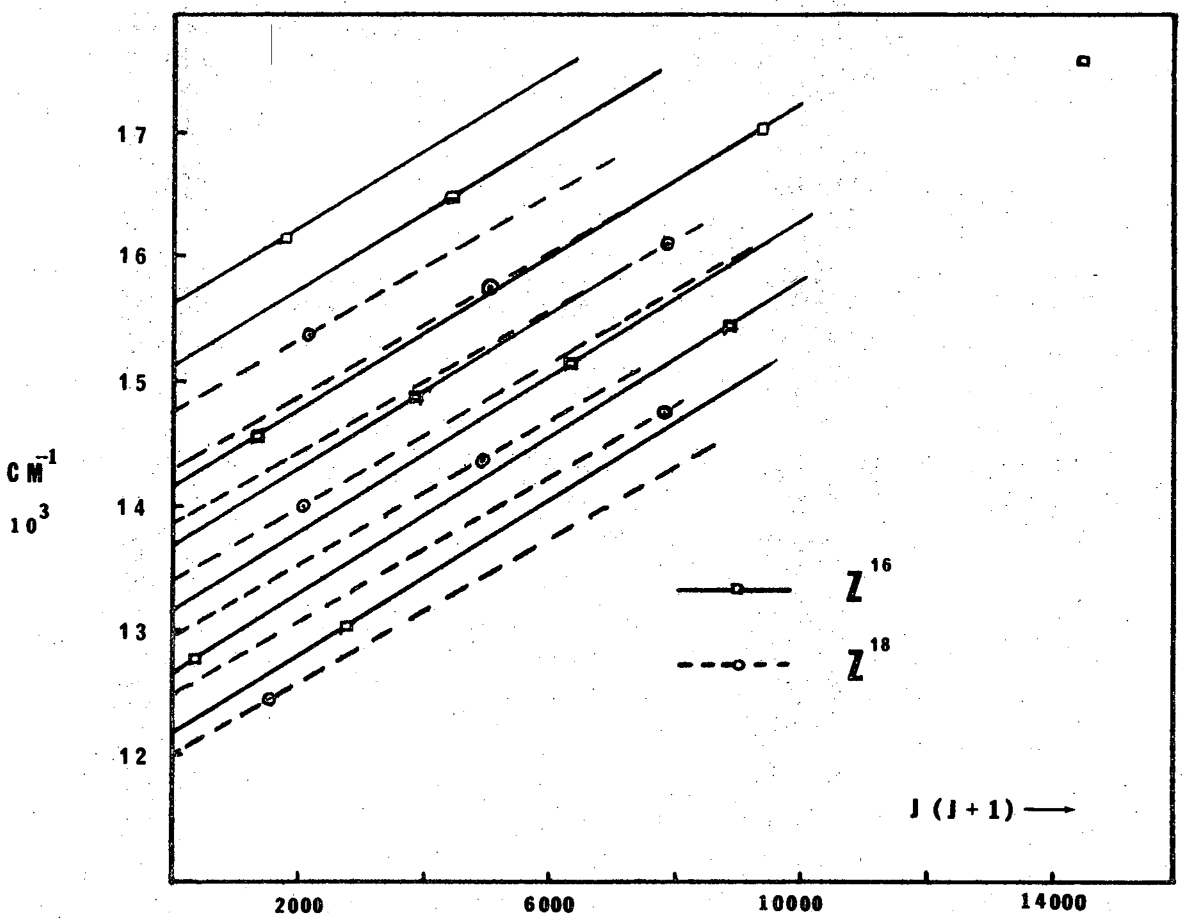


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Fig. 20. Plot of energy vs J(J+1) showing the vibrational levels of the Z^{16} and Z^{18} perturbing states.

IV. CORRELATION OF THE PERTURBING STATES OF CaO^{16} AND CaO^{18}

Hultin and Lagerqvist found six perturbing states in CaO^{16}, four called X, Y, Q and Z, having $B_v \sim 0.33$ and $\omega_e \sim 500$ and two, called A and B with $B_v \sim 0.38$ and $\omega_e \sim 600$. In CaO^{18} six perturbing states have also been found. However five of them have B_v values of 0.30 (comparable to 0.33 in CaO^{16}) and only one has a B_v value of .35 (comparable to 0.38 in CaO^{16}). The A^{16} state is indicated by only one overlapped perturbation near a region where a Q perturbation is expected but not observed. It is possible then that the B_v value estimated for A is incorrect and that the set of Z^{16} perturbations are really due to two perturbing states with $B_v \sim 0.33$. It is even possible that the A^{16} perturbation is really due to the missing (Q-1) level since other states predicted in this region could shift it without interacting with $A^1\Sigma$ (i.e. nine points of perturbation are possible between $^3\Pi$ and $^3\Sigma$ components in case (a), $^1\Delta$ is probably present but invisible to a $^1\Sigma$ state, etc. See Kovacs (1969) for a listing of possible interactions.) In this case the X^{16} or Y^{16} state may be due to two sets of perturbing levels.

First the two B-states, B^{16} and B^{18}, are correlated on the basis of their B_v-values. Using the $X^1\Sigma$ constants given in Hultin and Lagerqvist (1950), the first thirty levels of that state were calculated for CaO^{16} and CaO^{18} and compared to the B state. The results were encouraging and so the constants found in Brewer and Hauge (1968) (which are based on higher experimental values and therefore should be better in the region of interest) were also tried. The comparison is shown in Table 7. There is good agreement between the experimental and

and calculated values of B_v found at the same energy. Since B is the only perturbing state with B_v and ΔG values in this range, it is probably the $X^1\Sigma$ state. Since the four vibrational levels found correlate to V = 18, 19 in CaO^{16} and V = 20, 21 in CaO^{18}, the isotopic shift cannot be directly calculated. Extrapolated values for V^{18} = 18, 19 and V^{16} = 21 give isotopic shifts quite close to the calculated ones and a vibrational numbering which is only off by one quantum number. The V^{18}= 20 level appears to be perturbed.

The X^{18}, Y^{18}, Z^{18}, Q^{18}, W^{18}, and X^{16}, Y^{16}, Z^{16}, Q^{16} states will now be considered. The energy levels of CaO^{18} will be lower in energy than the corresponding levels in CaO^{16}. See Fig. 17 for example. If one compares the Y^{16} and Y^{18} electronic states, it is possible for $(Y^{16} + 3)$ to have the same vibrational quantum number as (Y^{18}), $(Y^{18} + 1)$, or $(Y^{18} + 2)$. In the following discussion, only the first two sets of levels lower in energy will be considered (i.e., $(Y^{16} + 1) \rightarrow (Y^{18})$, $(Y^{16} + 2) \rightarrow (Y^{18} + 1)$, $(Y^{16} + 3) \rightarrow (Y^{18} + 2)$, etc. and $(Y^{16} + 1) \rightarrow (Y^{18} + 1)$, $(Y^{16} + 2) \rightarrow (Y^{18} + 2)$, $(Y^{16} + 3) \rightarrow (Y^{18} + 3)$, etc). The sets at lower energies (i.e. $(Y^{16} + 2) \rightarrow (Y^{18})$ .... or $(Y^{16} + 3) \rightarrow (Y^{18})$ ... etc.) can also form possible combinations, however (since the isotopic shifts would be larger in this case) they would put the origins of the perturbing states at least 8000 cm^{-1} below $X^1\Sigma$ state. It is more important to check if these states are above or near $X^1\Sigma$ in order to determine the ground state of CaO. Also the larger the shifts, the harder it is to extrapolate to a meaningful v-value. It is important although to remember that lower origins are possible.

Since we have five CaO^{18} states, four CaO^{16} states, and two possibilities for each combination, there are forty ways to correlate the nine states. The comparison of Y^{16} with the next lowest set of Y^{18} levels will be called $(Y^{16}Y^{18})$; the comparison with the second lowest set $(Y^{16}Y^{18}d)$. The shifts calculated for all forty combinations are listed in Table A-1.

Equation (1) shows the relationship between v, $\omega_e x_e$, ω_e and the energy shifts. If the shifts are plotted vs v, the curve should intersect the x-axis at $v = -\frac{1}{2}$. At low v the slope is $\sim (\omega_e/(1-\rho))$: at higher v, the slope decreases in response to the $\omega_e x_e$ terms. The vibrational quantum numbers for any of the forty combinations mentioned can be obtained by plotting the shifts vs a relative v and extrapolating to zero. Figure 24 shows sample plots of the shift vs v for various values of $\omega_e x_e$ and ω_e. Similar plots were used as aids in extrapolating the experimental values. The plots for all the Y^{18} combinations are shown in Fig. 21.

Of the 40 combinations plotted, 28 were rejected. Table A-2 shows the comparisons. One of three reasons is given for rejecting a correlation.

(1) v_P too high. Same discussion as above applies here. These combinations are possible, but correlations giving states above $X^1\Sigma$ should be considered first.

(2) Scattered. Trends in energy away from the calculated shape of the curve (Fig. 24) were used as criteria, rather than one or two points being out of line. For example, an increase in slope at higher v-values (concave) would not be acceptable.

(3) $\omega_e x_e$ (a-b). ω_e and $\omega_e x_e$ values can be obtained from the shift vs v-plot and also from the energy separations of the vibrational

levels and the v-quantum numbers. If the values from these two methods do not agree, that correlation is rejected.

An example can best clarify this method. Consider the $(Q^{16}\ Y^{18})$ correlation. Various combinations of ω_e and $\omega_e x_e$ can fit the points. The lowest possible $\omega_e(\omega_e x_e = 0)$ value from the shift vs v plot can be obtained from the slope divided by $(1-\rho)$. (A higher ω_e is possible since $\omega_e x_e$ can decrease the slope, however a lower one is not for the same reason. $\omega_e x_e$ would only decrease the slope further.) In this case $\omega_e = 675$. The highest $\omega_e x_e$ which could be used is under ten. The quantum number for the Q^{16} level is v = 2. The difference between the v = 2 and v = 3 levels of Q^{16} is calculated from these constants as follows:

$$G(3.2) = \omega_e(3.5) - \omega_e x_e(3.5)^2 - \omega_2(2.5) + \omega_e x_e(2.5)^2$$

$$= \omega_e - 6\,\omega_e x_e = 675 - 6(10) = 615$$

The difference between the (Q^{16}) and $(Q^{16}+1)$ levels is 500 so this correlation is wrong. $\omega_e x_e$ would have to be 29 instead of 10 in order for ω_e to equal 675. A higher ω_e value would make G(3-2) still larger without substantially increasing the needed $\omega_e x_e$ value. The comment for this correlation in Table A-2 is $\omega_e x_e$(10-29) where 10 and 29 are the $\omega_e x_e$ values needed for the two methods.

Table 8(a) shows the 12 possible correlations left. If it is assumed that all the CaO^{18} states are used just once, then the $(X^{16}X^{18}d)$ correlation is correct. The Q^{16} state has a small matrix element in comparison to the X^{16}, Y^{16}, and Z^{16} states. It is unlikely to be correlated to more than one CaO^{18} state. Y^{18} can be combined with either Y^{16} or Q^{16}. The Y^{18} perturbations are much stronger than those of Q^{16} so the $(Y^{18}Y^{16})$ correlation appears to be the correct one. The Q^{16} and Z^{16} states both go to Q^{18} and Z^{18}. This is reasonable since the Q and Z perturbations are very close to each other in both isotopes. The Z perturbations are much stronger in both cases, which indicates combinations of $(Q^{16}Q^{18}d)$ and $(Z^{16}Z^{18}d)$. At this point all the CaO^{16} states and all the CaO^{18} states except W^{18} have been used. The three possible combinations using W^{18} are shown in Table 8(b) by dashed lines. Either $(X^{16}W^{18}d)$ or $(Y^{16}W^{18}d)$ would put W^{18} below $X^1\Sigma$ along with Q^{18}, Z^{18} and X^{18}. The $(Y^{16}W)$ correlation would put W^{18} at ~ 11080 cm^{-1}. The two possibilities for W^{18} are shown as dashed lines in Fig. 22. Among the states predicted to be in this region: $^3\Pi$, $^3\Sigma^-$, $^1\Pi$, $^1\Delta$, the following states or substates can perturb a $^1\Sigma^+$: $^3\Pi_1$, $^3\Pi_0$, $^1\Pi$, $^3\Sigma^-_{J+1}$, $^3\Sigma^-_{J-1}$. Assuming Hund's case (a) the five states should be grouped as two, two, one, since four of them are predicted to be substates of triplet electronic states. If W and Y are components of a triplet, the splitting would be on the order of 3000 cm^{-1}. This seems too large. (The doublet splitting in AsO, a much heavier molecule, is 1025 cm^{-1}. The splitting here would not be expected to be larger.) If $(Y^{16}W^{8})$ is not true, then W would be found at approximately -2500 cm^{-1} relative to $X^1\Sigma$. A summary of the perturbing states and their constants is found in Table 9 for the best correlations.

If any of the above assumptions are wrong, other sets of correlations become possible. The assumptions are:

(1) There is a one to one correlation between the states perturbing $A^1\Sigma$ in CaO^{16} and CaO^{18}.

(2) The perturbing states are $X^1\Sigma$, $^1\Pi$, $^3\Pi_0$, $^3\Pi_1$, $^3\Sigma_{J+1}$,

and $^3\Sigma^-_{J-1}$. These states are predicted to be low-lying by analogy to the isoelectronic C_2 states (Brewer, 1962), and are able to perturb a $^1\Sigma^+$ (Kovacs, 1969). A recent paper (Carlson, et al., 1970) suggests a low-lying $^3\Sigma^+$ state. The predicted $^1\Delta$ also would not perturb a $^1\Sigma$. Perturbations between a $^3\Sigma^+$ and a $^1\Sigma^+$ state are predicted to be very weak (Kovacs, 1969) and so it would be difficult to find an indication of $^3\Sigma^+$ in this study. Also six perturbing states and substates are predicted considering just $^3\Pi$, $^3\Sigma$, $^1\Pi$, and $X^1\Sigma$ perturbing states and six are found. If the $^3\Sigma^+$ state is included, one of the above states must be discredited, which would make it difficult to account for all of the sets of perturbations found. Two sets of perturbations are expected from both the $^3\Pi$ and the $^3\Sigma$ states, the $X^1\Sigma$ state is well assigned to the B-perturbing state, and the $^1\Pi$ state has low-lying counterparts in C_2, BeO, and MgO as well as coming from the same molecular orbital configuration as the $^3\Pi$ state. So it would be hard to re-assign just one of the perturbing sets of perturbations to a $^3\Sigma^+$. The two weak sets, B and Q, are easily correlated with $X^1\Sigma$ and $^3\Pi_1$. The perturbation at v' = 1, J = 57.9, which is assigned to the B^{18} state, is out of line however from the other B perturbations and might be due to a low $^3\Sigma^+$ state.

(3) The origin of the perturbing states is not below 8000 cm^{-1}. It is possible that this assumption is false and that lower origins exist. However since there are too many correlations giving lower values to be able to pick out a consistent set and because of the difficulty in extrapolating larger shifts, it is not possible to come to any definite conclusions.

(4) The $\omega_e x_e$ and the scattering criteria are assumed to be correct. There are at least three perturbing states below $X^1\Sigma$ if they are true.

(5) The splitting between $^3\Pi_0$ and $^3\Pi_1$ is less than 1000 cm^{-1}. This is based on a comparison of splittings found in other molecules (i.e. AsO, PO).

(6) The size of a perturbation will not change drastically with a change of isotope, i.e. $Q^{16} \rightarrow Q^{18}$.

All the assumptions appear to be reasonable. Also a supporting piece of evidence for the assignment in Table 9 is found in a low-temperature matrix isolation study of CaO (Wang, 1969). Bands were found starting at 20,367 cm^{-1} and identified as CaO by their isotope shift (CaO^{18}-CaO^{16}). The transition does not correspond to any known singlet transition and therefore indicates the possibility of a low-lying triplet state. It has been included in Fig. 23.

Also the splittings between states coming from the same molecular orbital configuration can be compared. For the ten-electron molecules (N_2, AlCl, etc.) the splittings between the $^3\Pi$ and $^1\Pi$ states from the $X\sigma\omega\Pi^4 V\Pi$ configuration are between 6000 - 16000 cm^{-1} for a wide range of molecular weights (Brewer, 1962). For the eight electron molecules the splitting between the $^1\Pi$ and $^3\Pi$ states of the $y\sigma^2 X\sigma\omega\pi^3$ configuration is 12000 cm^{-1} for CaO and 7600 cm^{-1} for C_2. This fits in quite well with our expectations from the ten-electron molecule case.

Table 7. Comparison of the B state and $X^1\Sigma$

	B State				$X^1\Sigma$ Calculated			
	ν	G(ν) cm^{-1}	ΔG	Bν	ν	G(ν) cm^{-1}	ΔG	Bν
CaO^{16}	B	12113	581	.381	18	12039	580	.382
	B + 1	12694			19	12619		
CaO^{18}	B	12650	672	~.35	20	12716	575	.348
	B + 1	13322		~.35	21	13268		.346

Table 8. Correlations Between the Perturbing States of CaO^{18} and CaO^{16}

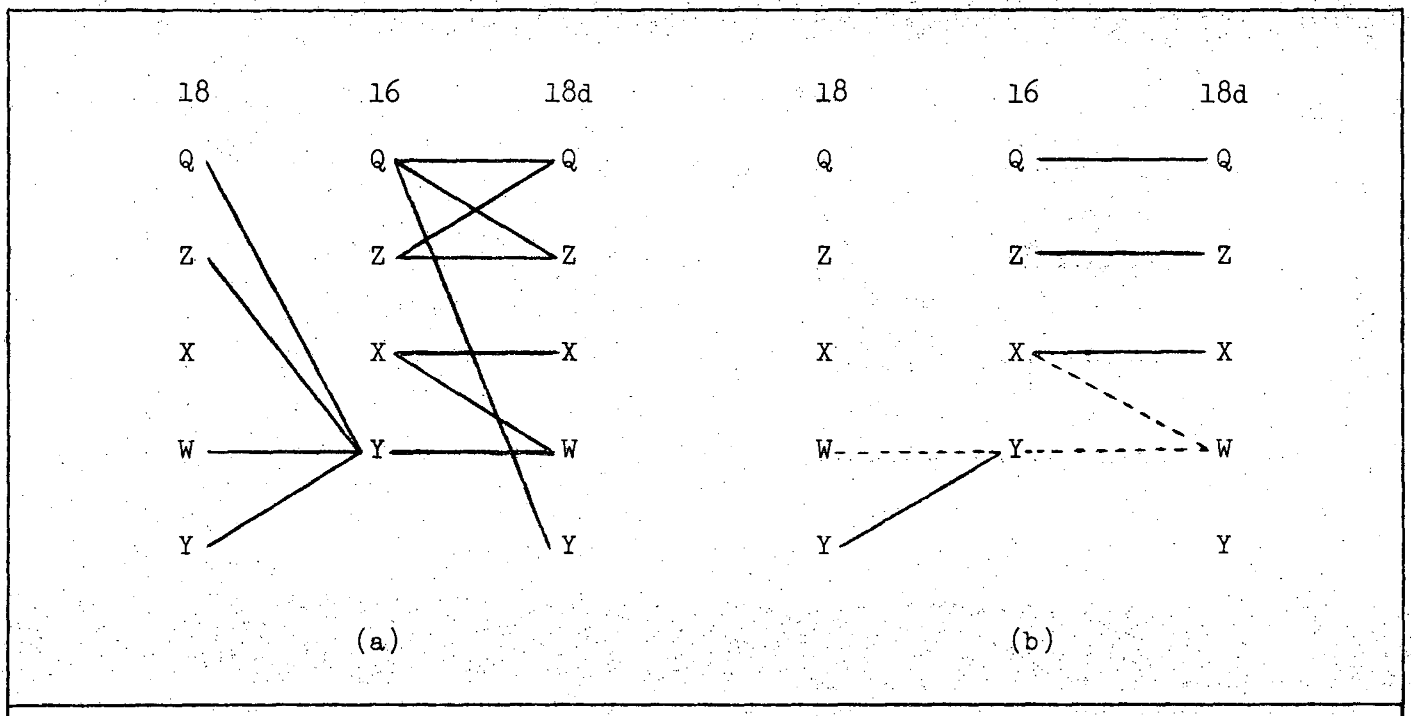

Table 9. Summary of Constants

State	Te	ωe	$\omega e x e$	Be	αe	D($\times 10^{-6}$)	re$\times 10^{8}$ cm
$A^1\Sigma$	11554.8	716	1.6	.4063	.0014	.54	1.906
Y($^1\Pi$?)	8080	490	~1.5	~.31			
$X^1\Sigma$	0	732.1	4.81	.4444	.0033	.658	1.822
X, W $\}$ $^3\Pi$; Z, Q $\}$ $^3\Sigma$?	~-3000	< 730					

Table 10. Predicted and Observed Transitions in CaO, 3500 - 12,000 Å

Transition	cm^{-1}	Å	Reference
$A^1\Sigma - X^1\Sigma$	11554.8	8660	Hultin and Lagerqvist, 1950
$B^1\Pi - {}^1\Pi$	17909	5580	
$B^1\Pi - {}^1\Delta$	~22000	~8300	
$B^1\Pi - A^1\Sigma$	24434	4100	
$B^1\Pi - X^1\Sigma$	25989	3848	Lagerqvist, 1954
$C^1\Sigma - {}^1\Pi$	20776	4810	
$C^1\Sigma - X^1\Sigma$	28855	3465	Lagerqvist, 1954
${}^3\Pi - {}^3\Pi$ or ${}^3\Sigma$	~21000	4760	Wang, 1969

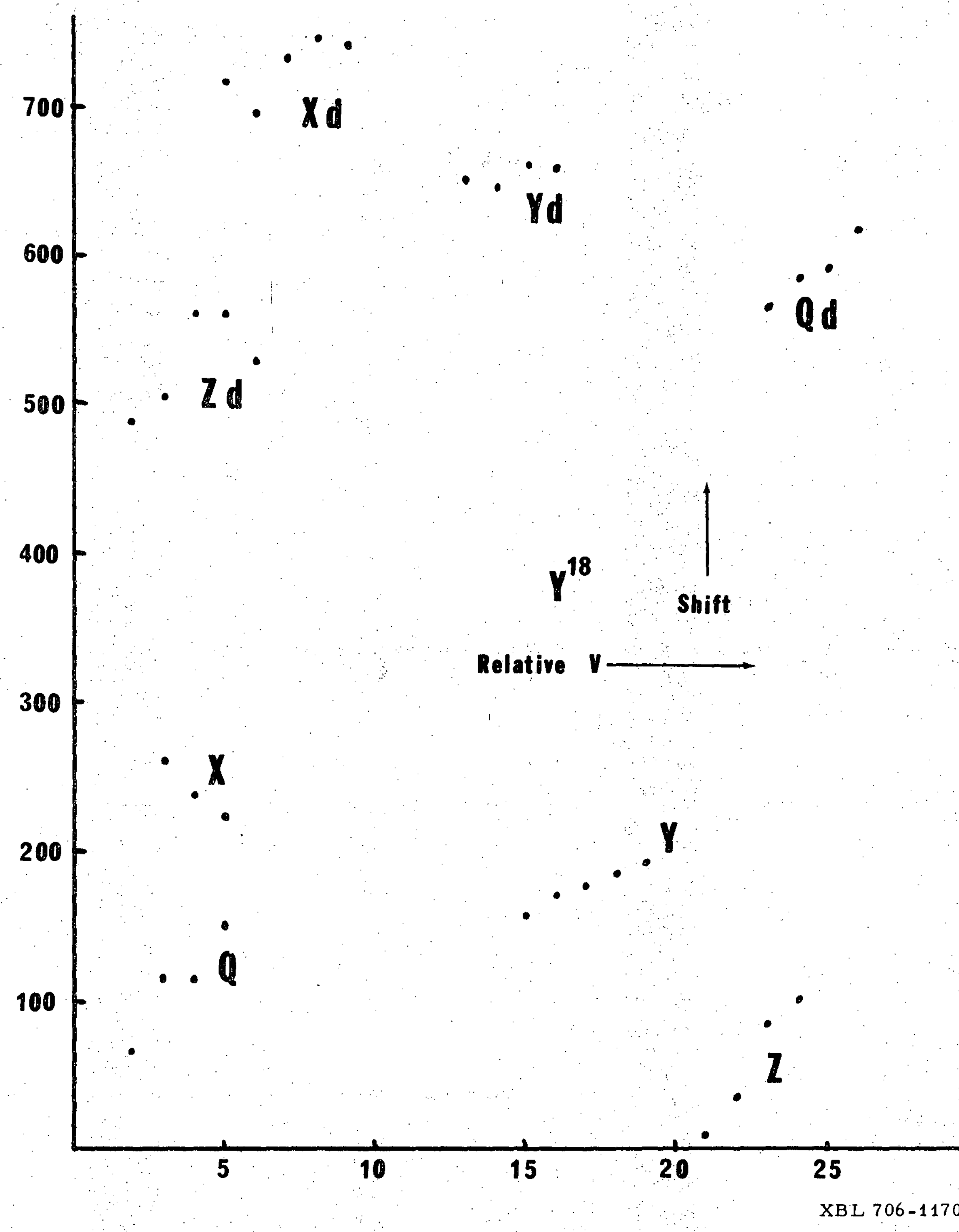

Fig. 21. Plot of the shift vs a relative vibrational numbering for all the correlations involving Y^{18}.

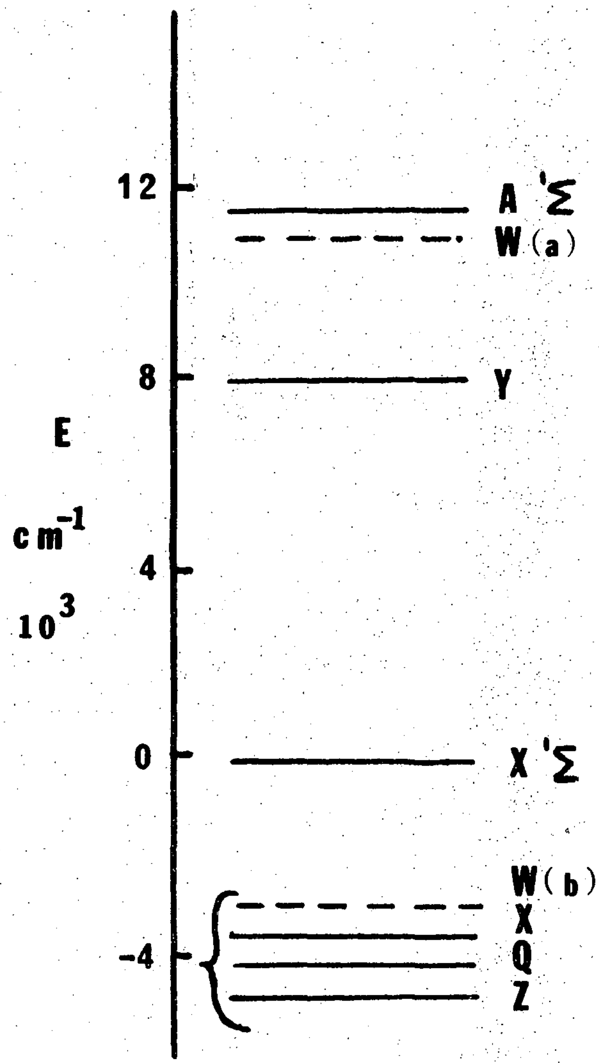

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Fig. 22. Relative energy scale for the perturbed and perturbing states.

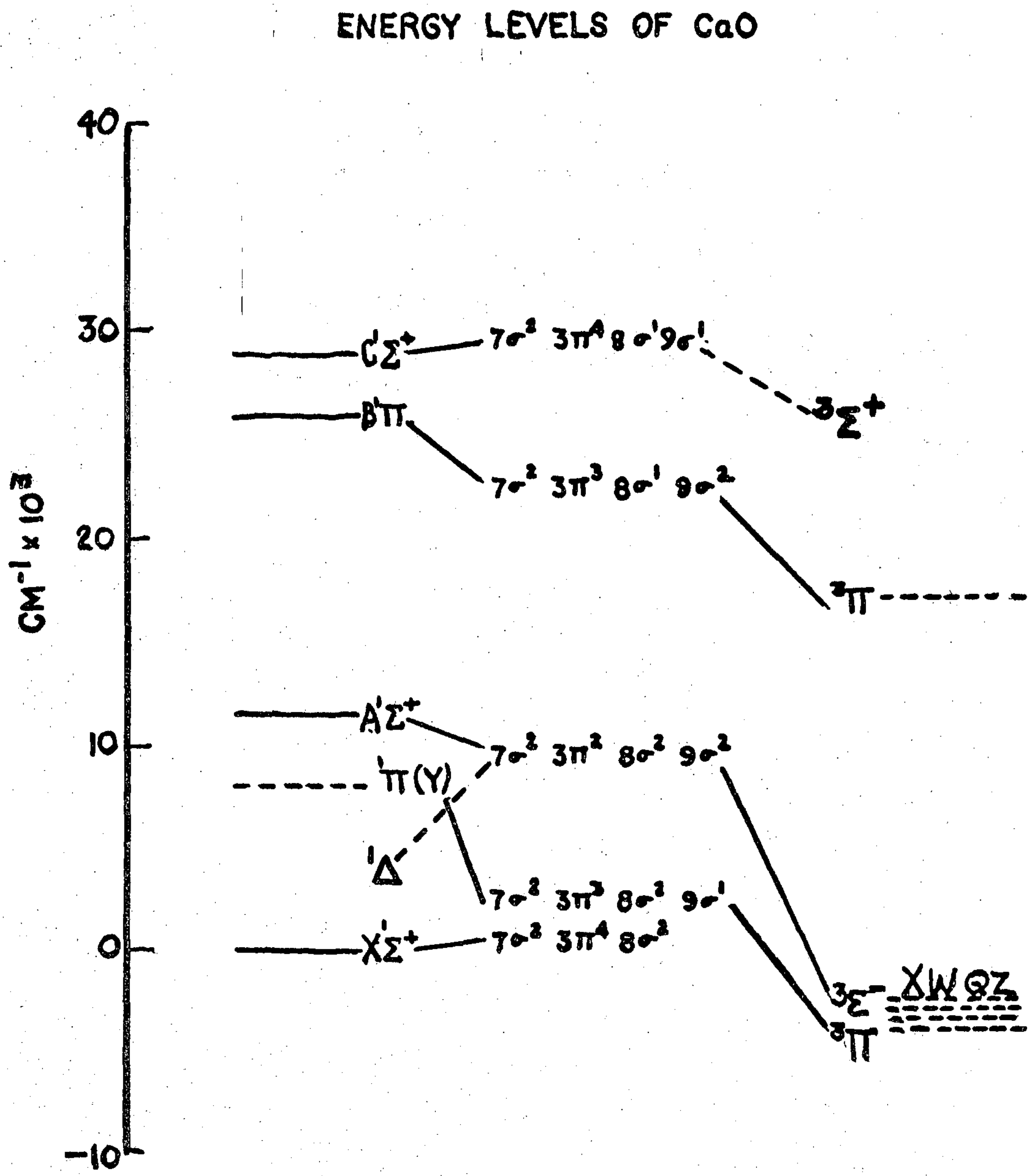

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Fig. 23. Low-lying energy levels of CaO.

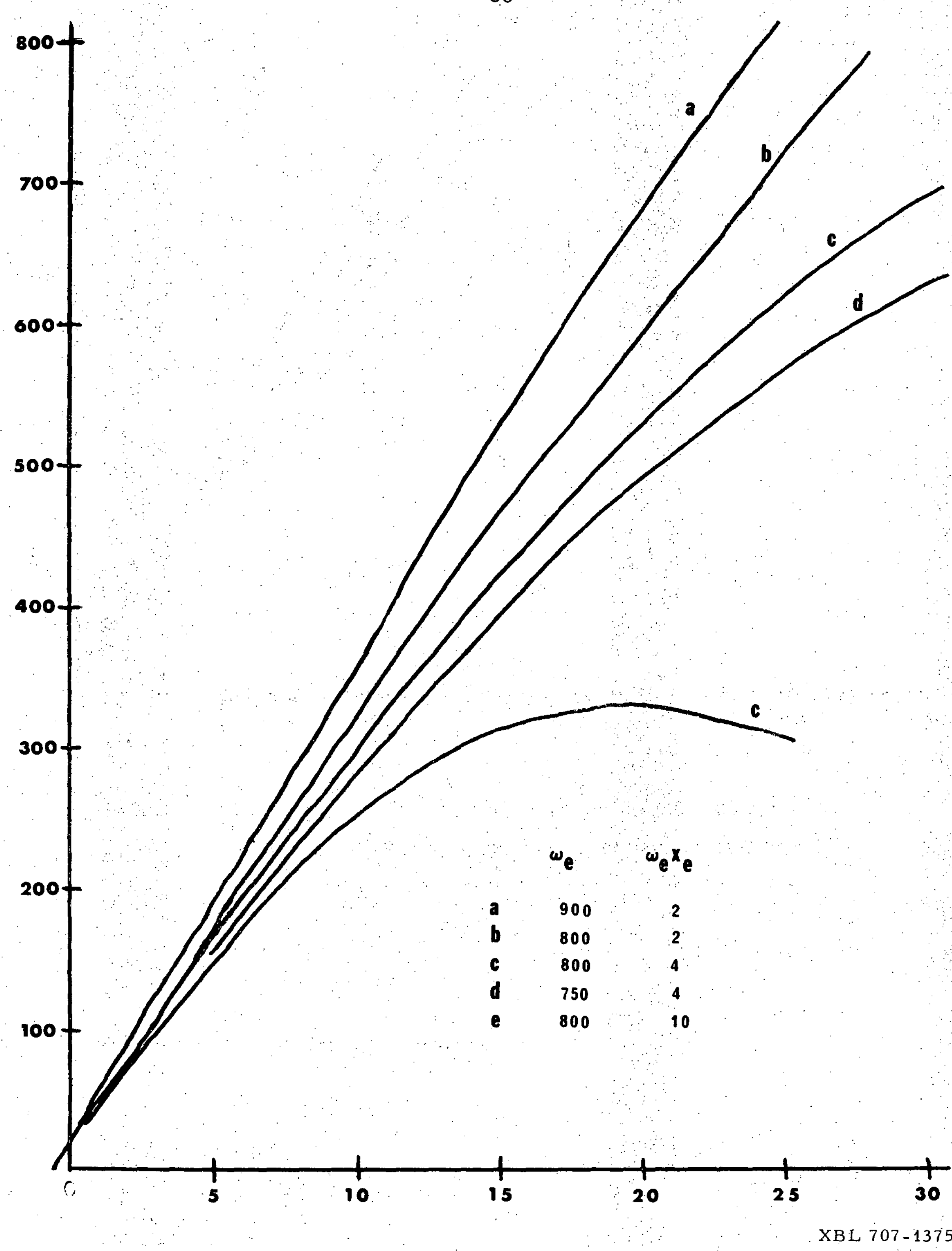

Fig. 24. Calculated plots of the vibrational isotopic shift vs the vibrational quantum number V for several combinations of ω_e and $\omega_e x_e$.

V. CONCLUSION

The above comparison of CaO^{16} and CaO^{18} perturbations gives a good qualitative description of some of the low-lying electronic states of CaO and shows that the $X^1\Sigma$ is not the ground state. It is hard to determine exact origins for X, Q, Z, and W because of the long extrapolations involved. The value given for all four is $-3000\ cm^{-1} \pm 2000\ cm^{-1}$. The Y state has a much shorter extrapolation and is found to be at $8080 \pm 500\ cm^{-1}$. Since the lowest $^1\Sigma^+$ state in C_2, BeO, and MgO has the largest ω_e value, the ω_e value for the X, Q, Z, Y, and W states is expected to be below 730.

The B state has been assigned to $X^1\Sigma$. However it is difficult to assign W, X, Q, Z and Y to specific states. Y should be a $^1\Pi$ since it stands by itself and the other possible singlet, $^1\Delta$, cannot perturb a $^1\Sigma$. Hultin and Lagerqvist (1950) indicate that X may be the $^3\Pi_0$ substate since its matrix element is independent of J. The Q perturbations are small and could be due to a $^3\Pi_1 - {}^1\Sigma^+$ interaction which has a small matrix element. That leaves W and Z to be assigned to $^3\Sigma_{J+1}$, and $^3\Sigma_{J-1}$.

It would be useful to determine the spectroscopic constants and origins of these states more accurately since the low-lying states of a molecule are needed for thermochemical calculations. Further experiments might include searching for calculated transitions (Table 10). For example, the $B^1\Pi$ - Y transition is predicted to be at ~ 5580 Å, quite close to a strong, unanalyzed system at 5555 Å. Another possibility, the molecular beam electric resonance technique used to measure the rotational constants of the ground state of BaO (Wharton and Klemperer, 1963), is probably not practical for CaO because of the difficulty of obtaining a CaO beam. Matrix fluorescence experiments could give the vibrational constants of the lower state of the transition found by Wang (1969). Electron spin resonance might also be done in a matrix to determine which is the lowest state, $^3\Pi$ or $^3\Sigma$ (Kasai, 1968). Also the perturbations of another isotopic molecule, such as $Ca^{44}O^{16}$, could be analyzed to confirm the correlations made in this paper.

APPENDIX A

COMPARISON OF CaO^{16} AND CaO^{18}

Table A-1. Shifts Between the Perturbing Vibrational Levels of CaO^{18} and CaO^{16}

	Y^{18}	$Y^{18}{}_d$	X^{18}	$X^{18}{}_d$	Q^{18}	$Q^{18}{}_d$	W^{18}	$W^{18}{}_d$	Z^{18}	$Z^{18}{}_d$
Z^{16}	-5 10 35 85 90	490 505 560 560 530	360 425 470 450 430 520 625	855 950 945 885 965	65 95 120 195 215	560 590 645 670 650	390 435 490 510 485 605 690	885 960 965 940 1020 1115	155 180 210 275 275 290 370 435	650 675 735 750 710 825 880
Q^{16}	85 115 115 150	565 585 590 615	5 25 5 50	435 505 500 505	170 200 225 270	635 670 675 725	15 45 65 105	465 515 520 565	255 290 305 330	725 755 765 805
Y^{16}	155 170 175 185 190	650 645 660 655	25 90 85 75 90	520 565 570 545	225 255 260 295 310	720 730 745 765	55 100 105 135 145	550 575 590 605	315 340 350 375 370	810 815 835 845
X^{16}	260 235 225 245	715 695 730 745 740	130 155 135 145 180 195 270 285	585 615 640 635 640 675 755 740	330 320 310 365 400	785 780 815 855 860	160 165 155 205 235 280 340	615 625 660 695 695 778	420 405 400 445 460 500	875 865 905 935

Table A-2. Comparison of Perturbing States: CaO^{16}, CaO^{18}

	X^{16}	Y^{16}	Q^{16}	Z^{16}
Y^{18}	scattered	maybe	ωexe (10-29)	ωexe (3-177)
$Y^{18}d$	Vp too high	Vp too high	maybe	scattering
X^{18}	scattered (concave)	scattered	scattered	scattered
$X^{18}d$	maybe	scattered	scattered	Vp too high
Q^{18}	scattered	maybe	ωexe (29-5)	ωexe(1-100)
$Q^{18}d$	Vp too high	scattered (concave)	maybe	maybe
W^{18}	scattered	maybe	ωexe (10-125)	ωexe(2-29)
$W^{18}d$	maybe	maybe	ωexe(1,15)	Vp too high
Z^{18}	scattered	maybe	ωexe(6,30)	ωexe(2-50)
$Z^{18}d$	Vp too high	Vp too high	maybe	maybe

APPENDIX B

This appendix contains the listings for the computer programs used to analyze the data. They were written for operation on the CDC computers at the Lawrence Radiation Laboratory at Berkeley. The program language is CDC's Chippewa Fortran which is nearly identical to Fortran IV.

1. STAND

Program STAND uses the measured spectral standard lines to calculate the wavelength and energy (cm^{-1}) for all the measured lines. Both the standard Th-lines and the CaO molecular lines were measured and recorded one to a card by a semi-automatic comparator (lent by Dr. John Phillips, University of California at Berkeley, Astronomy Department). Each card contained the relative position of the line, its relative intensity, and a code number indicating the type of line (standard, atomic, molecular, etc.)

The data deck consists of:

(a) TOY (I) indicates whether the measured line lies between 0-100 mm, 100-200 mm, or 200-300 mm on the measuring scale. The first data card reads -J1 with a 3A1 format.

(b) N, NLAST, and NU (format 3I5) where

N = order of fit +1

NU = number of standard lines

NLAST = the final value of N

(c) ETOL (format 8F10.5) is the tolerable error in calculating standard lines,

(d) SHIFT (format F10.2) relates the standard lines to the unknown lines. It is usually zero.

(e) Assigned standard line values YY(I) (format F10.3).

(f) Deck of measured lines, with all the standard lines first in the same order as their assigned values in (e).

(g) Blank card.

When N equals NLAST, one card is punched for each measured line with its wavelength, energy (cm^{-1}), relative intensity.

This program was written by David Green and Joel Tellinghuisen.

```
      PROGRAM STAND (INPUT,OUTPUT,PUNCH)
C     STAND TAKES MEASURED SPECTRAL STANDARD LINES AND CALCULATES
C          WAVELENGTH AND ENERGY (CM(-1)) FOR ALL MEASURED LINES
       DIMENSION TOY(3),BOY(1000),X(1000),Y(1000),STR (1000)
      DIMENSION    AA(10,10),YINV(1000), YY(200), B(10),DE(200)
       DIMENSION  INCA(1000)
      DIMENSION   COM(200), VW(1000)
      DIMENSION   XW(200),YYW(200)
        READ 800,TOY(1),TOY(2),TOY(3)
800     FORMAT (3A1)
801    READ1, N,NLAST,NU
1      FORMAT (3I5)
       PUN=0.0
       NSUB=N-NLAST
       IF (NSUB.EQ.0) PUN=1.0
       IF (NU.EQ.0)  GO TO 850
          NU1 = NU + 1
C     N=ORDER OF FIT +1,NU=NO. OF STANDARD LINES,NTOT=TOTAL NO. OF LINES
C     NLAST IS THE FINAL VALUE OF N
C     ETOL IS THE TOLERABLE ERROR IN CALCULATION OF STANDARD LINES
      READ 41, ETOL
   41 FORMAT(8F10.5)
      READ 855, SHIFT
855   FORMAT (F10.2)
 2    FORMAT (F10.1,F5.0)
 89   FORMAT (40F2.0)
 235  FORMAT (F10.1)
C     YY ARE THE STANDARD WAVE-LENGTHS
      READ 40, (YY(I),I=1,NU)
 40   FORMAT (F10.3)
        I=1
803    READ 42, INCA(I),BOY(I),X(I),STR(I)
   42 FORMAT(I6,5X,A1,F6.3,F6.1)
        PET =X(I)
        I=I+1
        IF(PET.NE.0.0) GO TO 803
       NTOT=I-2
        IF(BOY(1).EQ.TOY(3)) BET=200.
        IF(BOY(1).EQ.TOY(2)) BET=100.0
        IF (BOY(1) .EQ.TOY(1)) BET=0.0
        DO 804 I=1,NTOT
        IF (BOY(I) .EQ.TOY(1)) ADD=0.0
        IF(BOY(I).EQ.TOY(2)) ADD=100.0
        IF(BOY(I).EQ.TOY(3)) ADD=200.
        X(I)= X(I)+ADD
       DET=X(I)-BET
       IF(DET.GT.100.) X(I)=X(I)-100.
      BET=X(I)
804     CONTINUE
      DO 856 I = 1, NU
856   X(I)=X(I)+SHIFT
 1030     NW = NU
 200  NERR=0
      DO 53  I=1,NU
          XW(I) = X(I)
   53     YYW(I) = YY(I)
 103      N1 = N+1
```

```
         N2 = 2*N
      DO 5  NF = 2,N2
         F10 = SUMXN(NW,(NF-2),XW,YYW,2)
      DO 6  I=1,N
      DO 7  J=1,N
        IF ((I+J).EQ.NF)  17,7
   17    AA(I,J) = F10
    7 CONTINUE
    6 CONTINUE
    5 CONTINUE
      DO 11  I = 1,N
         J = I-1
   11    AA(I,N1) = SUMXN(NW,J,XW,YYW,1)
      CALL SOLVE(N,AA,B)
    3 FORMAT(8E15.6)
      PRINT 83
 83   FORMAT (1H1,3X*COEFFICIENTS OF POLYNOMIAL*//)
      PRINT 3,   (B(I),I=1,N)
      NM=N-1
      PRINT 71,NM
 71   FORMAT (    //3X*POLYNOMIAL ORDER IS*I3//3X*STANDARD LINES*//)
      PRINT 19
 19   FORMAT (//2X*MEASURED*4X*LAMBDA*4X*LAMBDA*2X*ERROR IN*6X*WAVE*/2X
     1*POSITION*6X*TRUE*5X*CALC.*4X*LAMBDA*3X*NUMBERS*//)
      DO 12  J = 1,NTOT
         Y(J) = YFUN(N,B,X(J))
 12   YINV(J)=1.E4/Y(J)
C     WAVE CONVERTS ANGSTROMS IN AIR TO WAVE NOS. IN VACUUM
      CALL WAVE(NTOT,YINV,VW)
      DO 13  J=1,NW
         Y(J) = YFUN(N,B,XW(J))
   13    YINV(J) = 1.E4/Y(J)
      CALL WAVE(NW,YINV,VW)
      DO 70  I=1,NW
   70    DE(I) = YYW(I) - Y(I)
  700 PRINT 20,  (XW(I),YYW(I),Y(I),DE(I),VW(I), I=1,NW)
 20   FORMAT (F10.3,3F10.3,F10.2)
      GO TO 701
      OMEGA = 0.0
         SN = NW
      C=N
C     OMEGA TELLS THE GOODNESS OF FIT...THE SMALLER THE BETTER
      DO 101  L=1,NW
         Q = (Y(L) - YYW(L))**2/(SN-C)
      OMEGA=OMEGA+Q
 101  CONTINUE
      PRINT 102,OMEGA
 102  FORMAT (//3X*OMEGA =*F10.5//)
C     THIS NEXT SECTION ELIMINATES ALL STANDARD LINES WHICH HAVE A
C     DIFFERENCE BETWEEN THE TRUE AND CALCULATED VALUES OF MORE THAN
C     ETOL ANGSTROMS
      L=1
      ERROR=ABS(DE(1))
      DO 72  I=2,NW
      IF  (ERROR.GE.ABS(DE(I)))  GO TO 72
      ERROR=ABS(DE(I))
      L=I
```

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```
 72     CONTINUE
        IF (ERROR.GE.ETOL)  GO TO 73
        GO TO 701
 73     L1=L+1
        NERR=NERR+1
        IF  (NERR.EQ.5)  GO TO 555
        DO 74  J=L1,NW
        J1=J-1
            TEMPO = YYW(J)
            YYW(J1) = TEMPO
            TEMPO = XW(J)
            XW(J1)= TEMPO
 74     CONTINUE
            NW = NW-1
            NS = NW-2
        IF (NLAST.EQ.NS)  GO TO 525
        GO TO 103
 555    PRINT 556
 556    FORMAT (1H1,3X*THERE ARE MORE THAN 5 ERRORS*//)
          GO TO 701
 525    PRINT 526
 526    FORMAT (//3X*THERE ARE TOO FEW GOOD LINES*//)
 701    PRINT 85
 85     FORMAT (    //3X*OBSERVATIONS*//2X*MEASURED*4X*LAMBDA*6X*WAVE*3X
      1*COMMENT*/2X*POSITION*5X*CALC.*3X*NUMBERS*//)
        PRINT 86,   (X(I),Y(I),VW(I),INCA(I),STR(I), I=NU1,NTOT)
   86 FORMAT(2F10.3,F10.2,I10,F6.1)
         IF(PUN.EQ.0.0) GO TO 880
        PUNCH 871,   (VW(I),Y(I),STR(I),INCA(I),X(I), I=1,NTOT)
  871 FORMAT(10X,3F10.2,I10,10X,F10.3)
880      CONTINUE
        N=N+1
 566    IF (N.LE.NLAST)  GO TO 1030
         GO TO 801
850      CONTINUE
        END
        FUNCTION SUMXN(NT,N,X,Y,JJ)
        DIMENSION    X(1000),Y(1000)
            S=0.0
          IF (JJ.EQ.1) 1,3
    1 DO 2  I=1,NT
    2       S = S + Y(I)*X(I)**N
          GO TO 20
    3 DO 4  I=1,NT
    4       S = S + X(I)**N
   20 SUMXN = S
        RETURN
        END
        SUBROUTINE SOLVE(N,A,B)
        DIMENSION  A(10,10),B(10)
            N1 = N+1
        DO 3  I=1,N
            ATEM = A(I,I)
        DO 4  J=1,N1
    4       A(I,J) = A(I,J)/ATEM
        DO 5  K=1,N
          IF (K-I) 51,5,51
```

```
   51     BTEM = A(K,I)
      DO 6  J=1,N1
    6     A(K,J) = A(K,J) - BTEM*A(I,J)
    5 CONTINUE
    3 CONTINUE
      DO 93  I=1,N
   93     B(I) = A(I,N1)
      RETURN
      END
      FUNCTION YFUN(N,B,Z)
      DIMENSION B(10)
          T = B(1)
      DO 1  I=2,N
          T = T + B(I)*Z**(I-1)
    1 CONTINUE
      YFUN = T
      RETURN
      END
      SUBROUTINE WAVE(NTOT,YINV,VW)
      DIMENSION    VW(1000),YINV(1000)
      DO 150  K=1,NTOT
      TE=0.
      T=YINV(K)
C     P IS THE REFRACTIVE INDEX OF WET AIR AT THIS WAVE-LENGTH
  151 P=((6432.8+2949810./(146.-T*T)+25540./(41.-T*T))*1.E-8)+1.
      T=YINV(K)/P
      IF ((ABS(TE-T)).LT.1.E-6) GO TO 152
      TE=T
      GO TO 151
  152 VW(K)=T*1.E4
  150 CONTINUE
      RETURN
      END
```

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2. <u>STNPLOT</u> uses the cards punched by program STAND to plot the measured lines on a graph of energy (cm^{-1}) vs relative intensity. The end of the deck is signaled by a card with 88 in columns 49 and 50. The dispersion in cm^{-1} per inch is given on the next card (format 8F10.5). See Figure (B-1) for a sample plot.

The program was written by Joel Tellinghuisen.

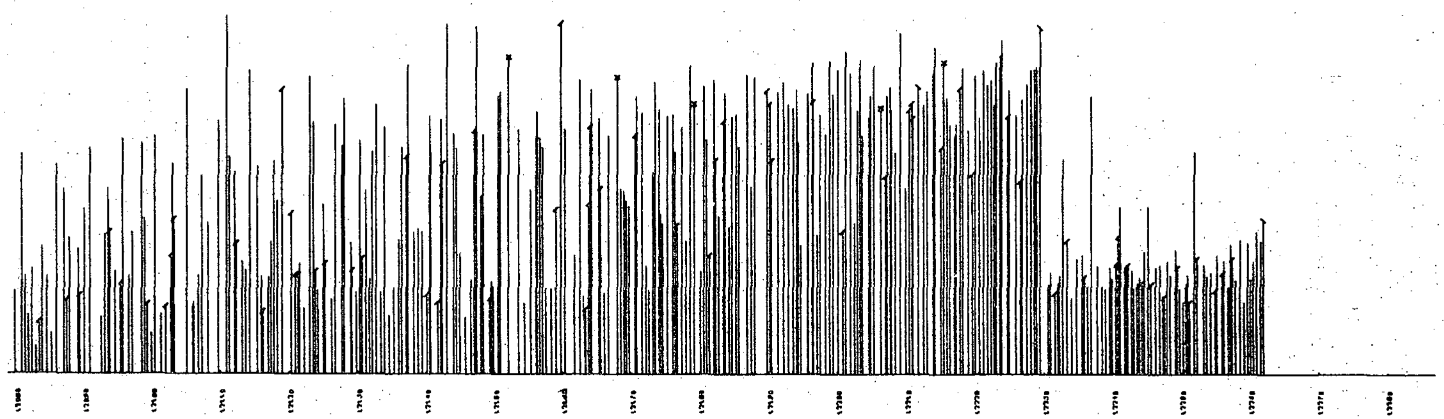

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Fig. B-1. Sample plot of energy (cm^{-1}) vs relative intensity from the program STN PLOT. Lines with bars slanting to the left ( ) indicate overlapped lines, bars slanting to the right ( ) red-degraded heads, and crosses ( ) two lines too close to be resolved.

```
      PROGRAM STNPLOT(INPUT,OUTPUT,TAPE98,PLOT,TAPE99=PLOT)
      DIMENSION  VW(1000),Y(1000),STR(1000),INCA(1000)
C     THE FOLLOWING CODE HAS BEEN USED FOR INCA.
C         0  AND  1    . . . ATOMIC LINES
C         2            . . . RED-DEGRADED BAND HEAD
C         3            . . . VIOLET-DEGRADED BAND HEAD
C         4            . . . SPIKE MEASURED ON CENTER
C    INTEGERS  5 THRU  0 RESULT IN NO SYMBOLS ON PLOTTED LINES.
    1 FORMAT(8F10.5)
    2 FORMAT(10X,3F10.2,I10)
    3 FORMAT(/////20X,*INPUT DATA*///)
    4 FORMAT(///*PLOT DISPERSION = *,F5.0,*  CM-1 PER INCH*///)
501     CONTINUE
      DO 11  I=1,1000
      READ 2,  VW(I),Y(I),STR(I),INCA(I)
        IF (INCA(I).EQ.88)  GO TO 12
   11 CONTINUE
   12     NTOT = I-1
      PRINT 3
      PRINT 2,  (VW(I),Y(I),STR(I),INCA(I),I=1,NTOT)
      READ 1,  DISP
      PRINT 4,  DISP
      CALL GRAPHX(VW,STR,INCA,NTOT,DISP)
       READ 500, ISTOP
500     FORMAT (I5)
       IF (ISTOP.NE.0) GO TO 501
      CALL CCEND
      END
      SUBROUTINE  GRAPHX(X,Y,IND,NT,DISP)
      COMMON/CCPOOL/XL,XH,YL,YH,CXL,CXH,CYL,CYH
      DIMENSION  X(500),Y(500),IND(500),XP(3),YP(3)
          XMIN = FMIN(NT,X)   $   XMAX = FMAX(NT,X)
          IA = XMIN/100. - 1
          IB = XMAX/100. + 1
          XL = 100.*IA   $   XH = 100.*IB
          DELTX = (XH-XL)/DISP*100.
          CXL = 100.   $   CXH = DELTX + 100.
          YA = FMIN(NT,Y)
              YL= 0.0    $    YH= 120. -YA
          CYL = 300.   $   CYH = 900.
          GL = DELTX/100. + .1
          NXL = GL
      CALL CCGRID(1,NXL,6HNOLBLS,1,6)
      CALL CCLBL(NXL,1)
      DO 11  I=1,NT
          XP(1) = X(I)   $  XP(2) = X(I)
             YP(1)= 105. -Y(I)    $        YP(2)=0.0
          NSYM = 0
        IF (IND(I).EQ.1)  NSYM = 8
        IF (IND(I).EQ.2)  NSYM = 4
        IF (IND(I).EQ.3)  NSYM = 5
        IF (IND(I).EQ.4)  NSYM = 2
      CALL CCPLOT(XP,YP,2,4HJOIN,NSYM,5)
   11 CONTINUE
      CALL CCNEXT
      RETURN
      END
```

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```
      FUNCTION  FMIN(N,X)
      DIMENSION  X(100)
        A = X(1)
      DO 10  I=1,N
        IF (X(I).LT.A)  A = X(I)
   10 CONTINUE
      FMIN = A
      RETURN
      END
      FUNCTION  FMAX(N,X)
      DIMENSION  X(100)
        B = X(1)
      DO 11  I=1,N
        IF (X(I).GT.B)  B = X(I)
   11 CONTINUE
      FMAX = B
      RETURN
      END
       SUBROUTINE CCLBL(NX1,NY1)                                         CCLBL
       COMMON/CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
       COMMON/CCFACT/FACTOR
       ISZERO=0
       XD=XMAX-XMIN            $YD=YMAX-YMIN
       CCXD=CCXMAX-CCXMIN      $CCYD=CCYMAX-CCYMIN
       XI=XD/FLOAT(NX1)        $YI=YD/FLOAT(NY1)
       KSIZE=1                 $KORIENT=1
C      LABEL FROM RIGHT TO LEFT ALONG THE X-AXIS.
       DO 2 NX=ISZERO,NX1
       CCX=CCXMAX-CCXD*FLOAT(NX)/FLOAT(NX1)
       X=(CCX-CCXMIN)*XD/CCXD+XMIN
C      SET X TO A TRUE ZERO IF X=0. TO WITHIN MACHINE ACCURACY.
       IF(ABS (X/XI).LT.1.0E-6)X=0.
      WRITE(98,28)X
2      CALL CCLTR(CCX+6.*FLOAT(KSIZE)/FACTOR,
     * CCYMIN-70.*FLOAT(KSIZE)/FACTOR,KORIENT,KSIZE)
       KSIZE=1                 $KORIENT=0
C      LABEL UPWARD ALONG THE Y-AXIS.
       DO 3 NY=ISZERO,NY1
       CCY=CCYMIN+CCYD*FLOAT(NY)/FLOAT(NY1)
       Y=(CCY-CCYMIN)*YD/CCYD+YMIN
C      SET Y TO A TRUE ZERO IF Y=0. TO WITHIN MACHINE ACCURACY.
       IF(ABS (Y/YI).LT.1.0E-6)Y=0.
       WRITE(98,27)Y
3      CALL CCLTR(CCXMIN-70.*FLOAT(KSIZE)/FACTOR,CCY,KORIENT,KSIZE)
27     FORMAT(E10.2)
   28 FORMAT(F7.0)
       RETURN
       END
```

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3. NOSORT calculates the combination differences, $\Delta_2 F''(J)$, for CaO^{18} from the spectroscopic constants of CaO^{16} and ρ. As illustrated in Figure B-2

$$\Delta_2 F''(J) = R(J-1) - P(J+1) = F_v''(J+1) - F_v''(J-1)$$

where $F_v''(J)$ is the energy of the J-rotational level of the lower vibrational state. Thus the energy difference between one line in the R-branch and one line in the P-branch is known. The energy of R(J-1) is calculated and every line in the region [SCAN + R(J-1)] to [R(J-1) - SCAN] is assumed to be a possible candidate for R(J-1). The combination difference $\Delta_2 F''(J)$ (IERR) is added to the possible R(J-1) lines and the program searches for P(J+1). If a pair of lines with the proper energy difference is found, a relative energy for the $F_v'(J)$ level (called EAVE) is calculated using the energies of P(J+1) and R(J-1) plus the spectroscopic constants of the lower vibrational state. All the EAVE's found for all the J values considered (JSTR<J<JEND) are plotted on a scale of relative energy vs J(J+1) (see Figure B-3). The quantity SL*J*(J+1) was substracted from EAVE so that the plot would be horizontal and graph paper not wasted. The numbers plotted in each case represent the relative intensities of the P-line, the A's indicate the calculated energy of P(J+1), and the circled numbers indicate combinations which have been assigned to the (0,0) band. Notice the perturbation at J 38.

A similar program is described in Kopp, et al., 1965.

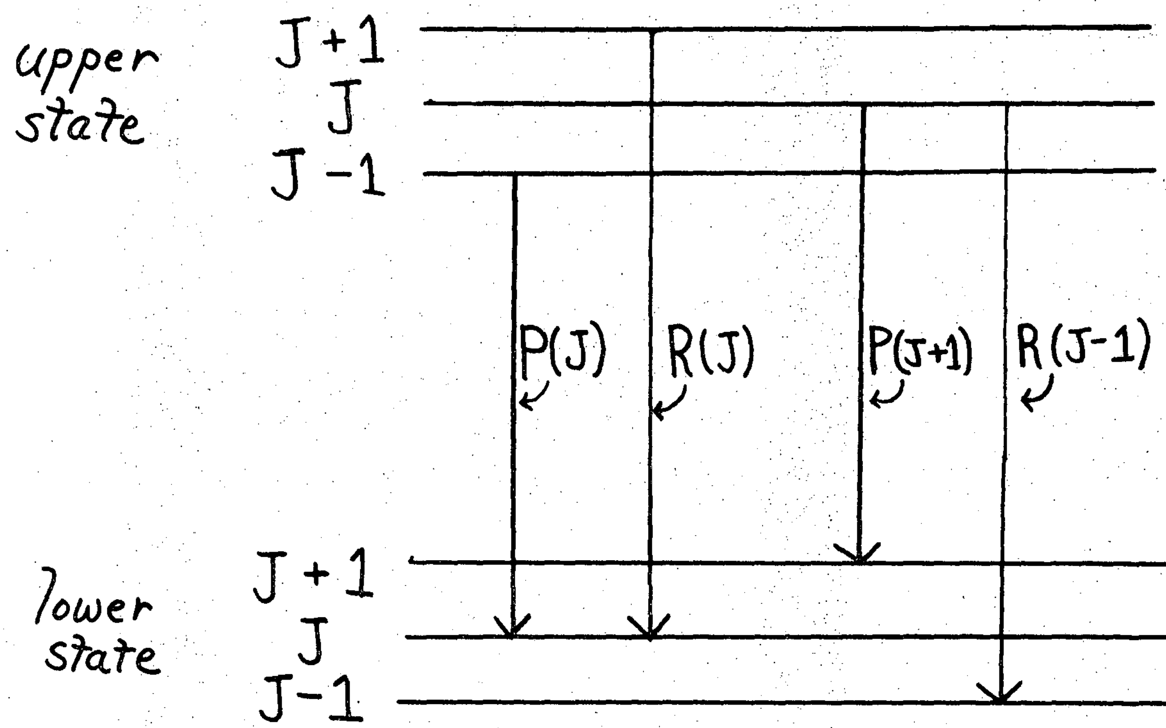


Fig. B-2. Plot illustrating the equations

$$\Delta_2''F(J) = R(J-1) - P(J+1) = F_V''(J+1) - F_V''(J-1)$$

$$\Delta_2'F(J) = R(J) - P(J) = F_V'(J+1) - F_V'(J-1)$$

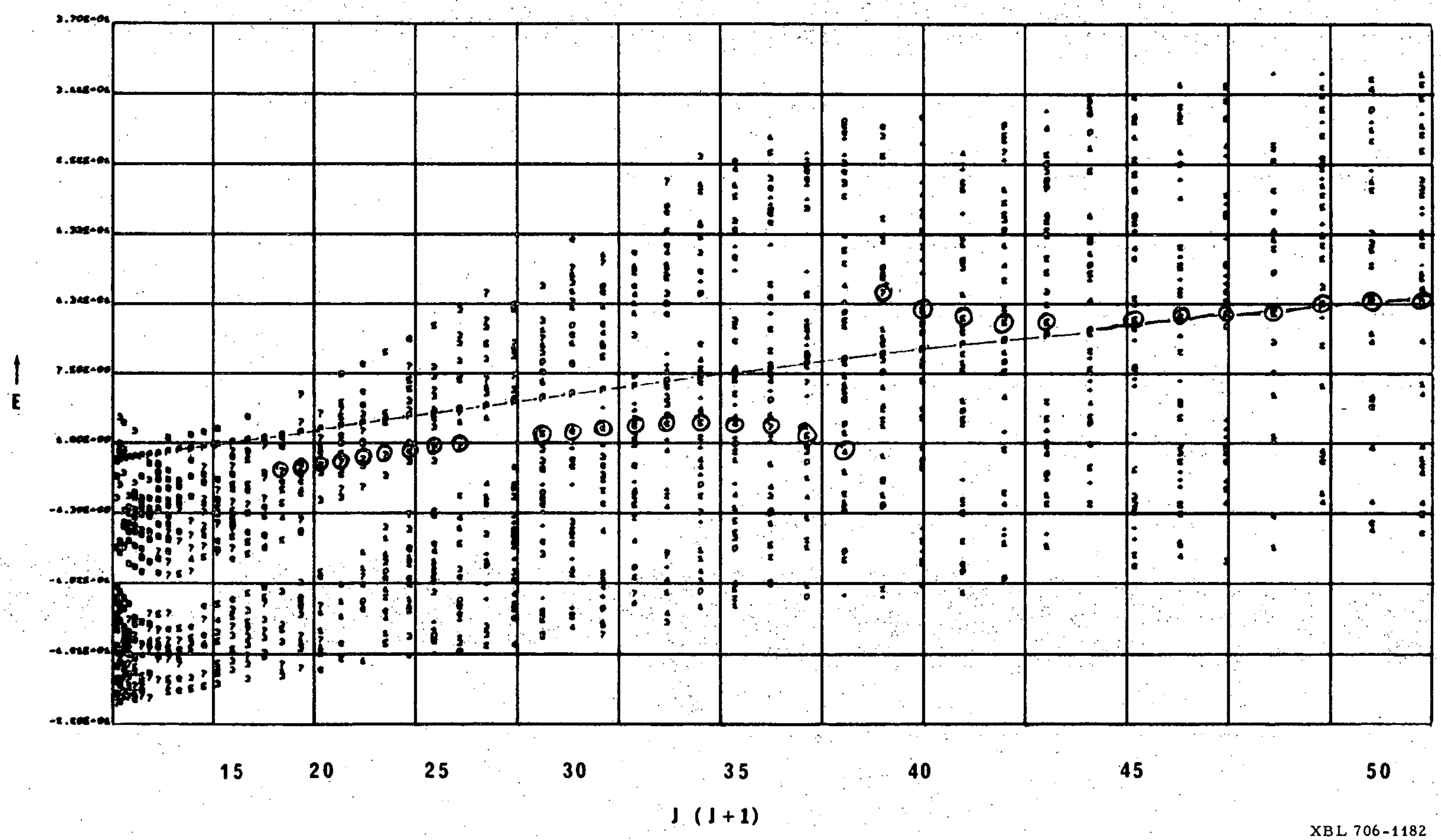


Fig. B-3. Sample plot of the program NOSORT. The coordinates are energy vs J(J+1). Each number represents a possible assignment of P(J+1) and R(J-1), the A's indicate the calculated energy of the J rotational level and the circled numbers show the combinations which have been assigned to the (0,0) band.

```
      PROGRAM NOSORT(INPUT,OUTPUT,TAPE98,PLOT,TAPE99=PLOT)
      DIMENSION   S(800),DEN(800),X(2500),Y(2500),SYM(2500),
     1  FV1(125),FV2(125),DIFF(125),R(125)
      INTEGER   SYM
      SL=.3669
      DISP=200.
      I=1
3     READ 120,S(I),DEN(I)
120   FORMAT (12X,F10.2,13X,F5.2)
      IF (S(I).EQ.0.0) GO TO 10
      I=I+1
      GO TO 3
10    ISPECT=I-1
     READ 14,TE1,OE1,OEXE1,OEYE1,BE1,AE1,DE1,BEE1,HE1,GE1,GEE1
     READ 14,TE2,OE2,OEXE2,OEYE2,BE2,AE2,DE2,BEE2,HE2,GE2,GEE2
 14  FORMAT (8F10.2)
      RHO = .959415
     OE1=RHO*OE1
     OEXE1=RHO**2*OEXE2
     OEYE1=OEYE1*RHO**3
     BE1=BE1*RHO**2
     AE1=AE1*RHO**3
     DE1=DE1*RHO**4
     BEE1=BEE1*RHO**5
     HE1=HE1*RHO**6
     GE1=GE1*RHO**7
     OE2=RHO*OE2
     OEXE2=RHO**2*OEXE2
     OEYE2=OEYE2*RHO**3
     BE2=BE2*RHO**2
     AE2=AE2*RHO**3
     DE2=DE2*RHO**4
     BEE2=BEE2*RHO**5
     HE2=HE2*RHO**6
     GE2=GE2*RHO**7
     PRINT 999,TE1,TE2,OE1,OE2,OEXE1,OEXE2,OEYE1,OEYE2,BE1,BE2,
    1AE1,AE2,DE1,DE2,BEE1,BEE2,HE1,HE2,GE1,GE2,GEE1,GEE2
 999 FORMAT (//3X*STATE 1*25X*STATE 2*///3X*TE=*F12.3,17X*TE=*F12.3//3X
    1*OE=*F12.3,17X*OE=*F12.3//3X*OEXE=*F10.4,17X*OEXE=*F10.4//3X
    2*OEYE=*F10.4,17X*OEYE=*F10.4//3X*BE=*F12.7,17X*BE=*F12.7//3X
    3*AE=*F12.8,17X*AE=*F12.8//3X*DE=*E12.4,17X*DE=*E12.4//3X*BEE=*
    4E11.4,17X*BEE=*E11.4//3X*HE=*E12.4,17X*HE=*E12.4//3X*GE=*E12.4,
    517X*GE=*E12.4//3X*GEE=*E11.4,17X*GEE=*E11.4//)
100   READ      14,ERR
      IF(ERR.EQ.0.0) GO TO 1000
      READ 14, SCAN
30    READ 2, V1,V2
 2   FORMAT  (3F10.5)
31    READ 701 ,JSTR,JEND
 701 FORMAT (2I10)
      PRINT 41,V2,V1
41    FORMAT (1H1*DATA FOR V',V''* 2F5.1)
      PRINT 787, SL
787    FORMAT(2X*SL=*F10.5)
     C=V1+.5
     D=V2+.5
      V00=TE2-TE1+OE2*D-D**2*(OEXE2-D*OEYE2)-OE1*C+C**2*(OEXE1-C*OEYE1)
```

XBL 707-1396

```
     1 +7.2525
        BV1= BE1-AE1*C
        DV1=DE1+BEE1*C
        HV1=HE1-GE1*C
        BV2= BE2-AE2*D
        DV2= DE2-BEE2*D
        HV2=HE2-GE2*D
        DO 20  J  = JSTR , JEND
         A=J
         F=A+1.0
         FV1(J)=BV1*A*F-DV1*(A*F)**2
         FV2(J)=BV2*A*F-DV2*(A*F)**2
 20     CONTINUE
        JAZZ = JEND -1
        DO 35  J = JSTR,JAZZ
        R(J)= V00+FV2(J+1) -FV1(J)
 35     CONTINUE
         JSTOP=JEND-2
         DO 5 I =JSTR,JSTOP
         J1=I+1
         J2=I+2
5        DIFF(J1)=FV1(J2)-FV1(I)
         PRINT 6
6        FORMAT (2H1 *J*7X*DIFF*9X*TRUE*9X*P LINE*7X*INT P *7X*R LINE*7X*
     1INT R*7X*ENERGY*5X*E-DIFF*)
         NO=0
         JO=       JSTR+1
         DO 7 I=JO,JSTOP
         NO=NO+1
         IF(NO.GT.2500) GO TO 29
         SYM(NO)=1HA
         X(NO)=I*(I+1)
         Y(NO)=FV2(I)-SL*X(NO)
         PRINT114,I,DIFF(I),FV2(I)
114      FORMAT(2X,I5,3X,F10.2,3X,F10.2)
          PRINT 19,X(NO),Y(NO)
         SC1=R(I-1)+SCAN
         SC2=R(I-1)-SCAN
         DO 8 IN=1,ISPECT
         IF (S(IN).LE.SC1) GO TO 11
8        CONTINUE
11       JSCAN1= IN
         DO 9 IT=IN,ISPECT
         IF (S(IT).LE.SC2) GO TO 13
9        CONTINUE
13       JSCAN2= IT
          DO 12 J= JSCAN1,JSCAN2
         E1=S(J)-DIFF(I)+ERR
         E2=E1-2.0*ERR
         DO 15 N = J,ISPECT
         IF(S(N).LT.E1) GO TO 101
         GO TO 15
101      IF(S(N).LT.E2) GO TO 12
         NO=NO+1
          IF (NO.GT.2500) GO TO 29
         EP=S(N)-V00+FV1(I+1)
         ER=S(J)-V00+FV1(I-1)
         X(NO)=I*(I+1)
         EAVE=(ER+EP)/2.0
```

XBL 707-1397

```
      EDIFF=EAVE- FV2(I)
      Y(NO)=EAVE-SL*X(NO)
      NDEN=(DEN(N)+5.0)*.1
      SYM(NO)=10-NDEN
      SYM(NO)=SYM(NO)+33B
      SYM(NO)=LEFT(SYM(NO),54)
      PRINT 19 ,S(N),DEN(N),S(J),DEN(J),EAVE,EDIFF,Y(NO)
19    FORMAT (33X,7(3X,F10.2))
15    CONTINUE
12    CONTINUE
7     CONTINUE
      GO TO 40
29    NO=NO-1
40    CALL GRAPH(X,Y,SYM,NO,DISP)
      GO TO 100
1000  CONTINUE
     CALL CCEND
      END
      SUBROUTINE GRAPH( X,Y,SYM,NT,DISP)
     COMMON/CCPOOL/XL,XH,YL,YH,CXL,CXH,CYL,CYH
      DIMENSION X(3750),Y(3750),SYM(3750)
         XMIN = FMIN(NT,X)  $  XMAX = FMAX(NT,X)
         IA = XMIN/100. - 1
         IB = XMAX/100. + 1
         XL = 100.*IA  $  XH = 100.*IB
         DELTX = (XH-XL)/DISP*100.
         CXL = 100.  $  CXH = DELTX + 100.
      YMIN=FMIN(NT,Y)  $  YMAX=FMAX(NT,Y)
      IA=YMIN-2.0
      IB=YMAX+2.0
      YL=IA
      YH=IB
      CYL=200.  $CYH= 900.
         GL = DELTX/100. + .1
         NXL = GL
      NYL=10
      CALL CCGRID (NXL,6HLABELS,NYL)
      DO 11 I=1, NT
      YP= (Y(I)-YL)*(CYH-CYL)/(  YH-YL)+CYL
      XP=(X(I)-XL)*(CXH-CXL)/(XH-XL)+CXL
      CALL CCLTR(XP,YP,0,1,SYM(I),1)
11    CONTINUE
     CALL CCNEXT
     RETURN
     END
     FUNCTION  FMIN(N,X)
     DIMENSION  X(100)
        A = X(1)
     DO 10  I=1,N
       IF (X(I).LT.A)  A = X(I)
  10 CONTINUE
     FMIN = A
     RETURN
     END
     FUNCTION  FMAX(N,X)
     DIMENSION  X(100)
        B = X(1)
     DO 11  I=1,N
       IF (X(I).GT.B)  B = X(I)
  11 CONTINUE
     FMAX = B
     RETURN
     END
```

XBL 707-1398

4. BOTH is basically the same program as NOSORT only after an R(J-1) and P(J+1) is found to satisfy the lower state combination difference, a P(J-1) must also be found to satisfy the upper state combination difference for (J-1). The upper state differences (DI) are read in by statement 38.

```
      PROGRAM BOTH (INPUT,OUTPUT,TAPE98,PLOT,TAPE99=PLOT)
      DIMENSION   S(800),DEN(800),X(2500),Y(2500),SYM(2500),
     1   FV1(125),FV2(125),DIFF(125),R(125)
      DIMENSION DIF(125)
      INTEGER   SYM
      SL=.3655
      DISP=200.
      I=1
3     READ 120,S(I),DEN(I)
12    FORMAT (12X,F10.2,13X,F5.2)
      IF (S(I).EQ.0.0) GO TO 10
      I=I+1
      GO TO 3
10    ISPECT=I-1
      READ 14,TE1,OE1,OEXE1,OEYE1,BE1,AE1,DE1,BEE1,HE1,GE1,GEE1
      READ 14,TE2,OE2,OEXE2,OEYE2,BE2,AE2,DE2,BEE2,HE2,GE2,GEE2
14    FORMAT (8F10.2)
      RHO = .959415
      OE1=RHO*OE1
      OEXE1=RHO**2*OEXEK
      OEYE1=OEYE1*RHO**3
      BE1=BE1*RHO**2
      AE1=AE1*RHO**3
      DE1=DE1*RHO**4
      BEE1=BEE1*RHO**5
      HE1=HE1*RHO**6
      GE1=GE1*RHO**7
      OE2=RHO*OE2
      OEXE2=RHO**2*OEXE2
      OEYE2=OEYE2*RHO**3
      BE2=BE2*RHO**2
      AE2=AE2*RHO**3
      DE2=DE2*RHO**4
      BEE2=BEE2*RHO**5
      HE2=HE2*RHO**6
      GE2=GE2*RHO**7
      PRINT 999,TE1,TE2,OE1,OE2,OEXE1,OEXE2,OEYE1,OEYE2,BE1,BE2,
     1AE1,AE2,DE1,DE2,BEE1,BEE2,HE1,HE2,GE1,GE2,GEE1,GEE2
999   FORMAT (//3X*STATE 1*25X*STATE 2*///3X*TE=*F12.3,17X*TE=*F12.3//3X
     1*OE=*F12.3,17X*OE=*F12.3//3X*OEXE=*F10.4,17X*OEXE=*F10.4//3X
     2*OEYE=*F10.4,17X*OEYE=*F10.4//3X*BE=*F12.7,17X*BE=*F12.7//3X
     3*AE=*F12.8,17X*AE=*F12.8//3X*DE=*E12.4,17X*DE=*E12.4//3X*BEE=*
     4E11.4,17X*BEE=*E11.4//3X*HE=*E12.4,17X*HE=*E12.4//3X*GE=*E12.4,
     517X*GE=*E12.4//3X*GEE=*E11.4,17X*GEE=*E11.4//)
100   READ     14,ERR
      IF(ERR.EQ.0.0) GO TO 1000
      READ 14,ERR2
      READ 14, SCAN
30    READ 2, V1,V2
2     FORMAT  (3F10.5)
31    READ 701 ,JSTR,JEND
701   FORMAT (2I10)
      PRINT 41,V2,V1
41    FORMAT (1H1*DATA FOR V','V''* 2F5.1)
      PRINT 752,ERR,ERR2
752   FORMAT (1X,2F10.3)
      PRINT 787, SL
787   FORMAT (2X*SL=*F10.5)
      C=V1+.5
      D=V2+.5
```

XBL 707-1399

```
      V00=TE2-TE1+OE2*D-D**2*(OEXE2-D*OEYE2)-OE1*C+C**2*(OEXE1-C*OEYE1)
     1 +7.2525
        BV1= BE1-AE1*C
      DV1=DE1+BEE1*C
      HV1=HE1-GE1*C
      BV2= BE2-AE2*D
      DV2= DE2-BEE2*D
      HV2=HE2-GE2*D
      DO  20  J  = JSTR , JEND
       A=J
       F=A+1.0
       FV1(J)=BV1*A*F-DV1*(A*F)**2
       FV2(J)=BV2*A*F-DV2*(A*F)**2
   20 CONTINUE
      JAZZ = JEND -1
      DO 35  J = JSTR,JAZZ
      R(J)= V00+FV2(J+1) -FV1(J)
   35 CONTINUE
       JSTOP=JEND-2
        DO 5 I=JSTR,JSTOP
        J1=I+1
        J2=I+2
    5   DIFF(J1)=FV1(J2)-FV1(I)
       NO=0
   42  NA=0
       JAP=0
   38 READ37,JA,DI
   37 FORMAT (I5,F10.5)
      TOP=JA+DI
      IF(TOP.EQ.0.0)  GO TO 39
      NA=NA+1
      IF(NA.EQ.1) JO=JA+1
      DIF(JA)=DI
      JAP=JA
      GO TO 38
   39 JSTOP=JAP+1
       IF(JAP.EQ.0) GO TO 1000
       PRINT 6
    6 FORMAT (1X*J*25X*P(J+1)*7X*INT P*7X*R(J-1)* 7X*INT R*7X*ET-EC*
     1 7X*DIF LOW*7X*DIF UP*7X*P(J-1)*)
       DO 7 I=JO,JSTOP
       NO=NO+1
       IF(NO.GT.2500) GO TO 29
       SYM(NO)=1HA
       X(NO)=I*(I+1)
       Y(NO)=FV2(I)-SL*X(NO)
      PRINT 114,I,DIFF(I),FV2(I),DIF( I-1)
  114 FORMAT (2X,I5,3(3X,F10.2))
        PRINT 19,X(NO),Y(NO)
       SC1=R(I-1)+SCAN
       SC2=R(I-1)-SCAN
       DO 8 IN=1,ISPECT
       IF (S(IN).LE.SC1) GO TO 11
    8  CONTINUE
   11  JSCAN1= IN
       DO 9 IT=IN,ISPECT
       IF (S(IT).LE.SC2) GO TO 13
```

XBL 707-1400

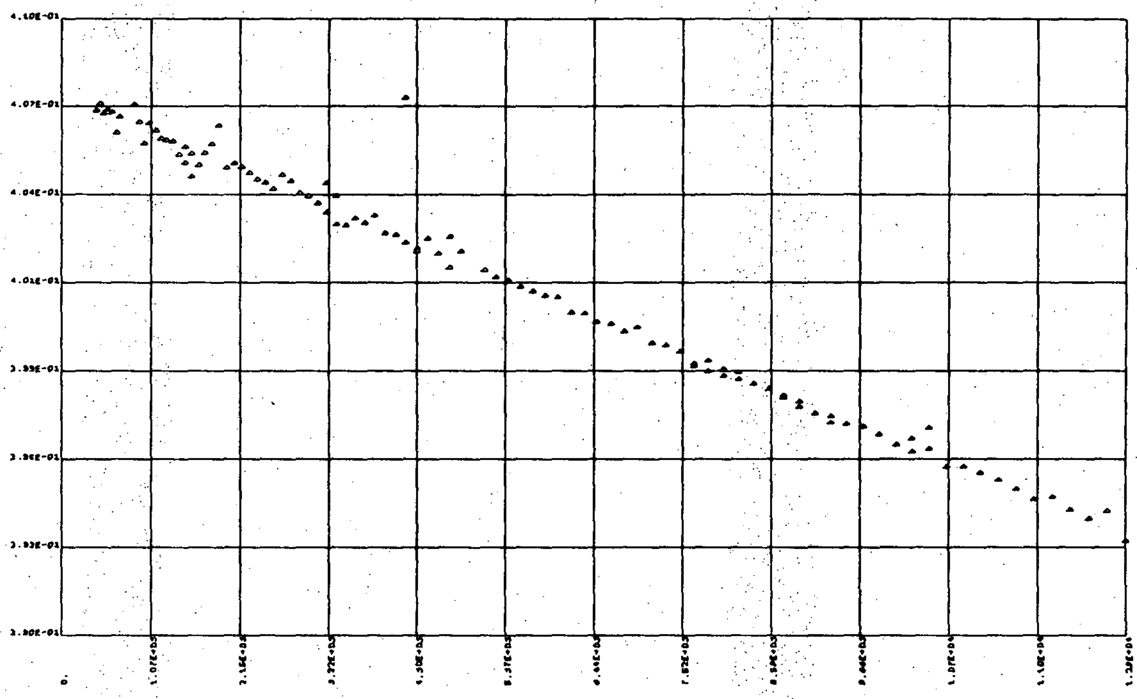
```
9       CONTINUE
13      JSCAN2= IT
         DO 12 J= JSCAN1,JSCAN2
        E1=S(J)-DIFF(I)+ERR
        E2=E1-2.0*ERR
        DO 15 N = J,ISPECT
        IF(S(N).LT.E1) GO TO 101
        GO TO 15
101     IF(S(N).LT.E2) GO TO 12
       E3=S(J)-DIF(I-1)+ERR2
       E4=E3-2.0*ERR2
       DO 16 NU=J,ISPECT
       IF (S(NU).LT.E3) GO TO 102
       GO TO 16
102     IF (S(NU).LT.E4) GO TO 15
       UP=S(J)-S(NU)
       BOT=S(J)-S(N)
        NO=NO+1
         IF (NO.GT.2500) GO TO 29
        EP=S(N)-V00+FV1(I+1)
        ER=S(J)-V00+FV1(I-1)
        X(NO)=I*(I+1)
        EAVE=(ER+EP)/2.0
        EDIFF=EAVE- FV2(I)
        Y(NO)=EAVE-SL*X(NO)
        NDEN=(DEN(N)+5.0)*.1
        SYM(NO)=10-NDEN
        SYM(NO)=SYM(NO)+33B
        SYM(NO)=LEFT(SYM(NO),54)
       PRINT 19,S(N),DEN(N),S(J),DEN(J),EDIFF,BOT, UP,S(NU)
19     FORMAT (20X,8(3X,F10.2))
16     CONTINUE
15      CONTINUE
12      CONTINUE
7       CONTINUE
         GO TO 42
1000    CONTINUE
        GO TO 40
29      NO=NO-1
40      CALL GRAPH(X,Y,SYM,NO,DISP)
       CALL CCEND
        END
        SUBROUTINE GRAPH( X,Y,SYM,NT,DISP)
       COMMON/CCPOOL/XL,XH,YL,YH,CXL,CXH,CYL,CYH
        DIMENSION X(3750),Y(3750),SYM(3750)
           XMIN = FMIN(NT,X)  $  XMAX = FMAX(NT,X)
           IA = XMIN/100. - 1
           IB = XMAX/100. + 1
           XL = 100.*IA  $  XH = 100.*IB
           DELTX = (XH-XL)/DISP*100.
           CXL = 100.  $  CXH = DELTX + 100.
        YMIN=FMIN(NT,Y)  $  YMAX=FMAX(NT,Y)
        IA=YMIN-2.0
        IB=YMAX+2.0
        YL=IA
        YH=IB
        CYL=200.  $CYH= 900.
           GL = DELTX/100. + .1
           NXL = GL
```

XBL 707-1401

```
      NYL=10
      CALL CCGRID (NXL,6HLABELS,NYL)
      DO 11 I=1, NT
      YP= (Y(I)-YL)*(CYH-CYL)/(  YH-YL)+CYL
      XP=(X(I)-XL)*(CXH-CXL)/(XH-XL)+CXL
      CALL CCLTR(XP,YP,0,1,SYM(I),1)
11    CONTINUE
      CALL CCNEXT
      RETURN
      END
      FUNCTION  FMIN(N,X)
      DIMENSION  X(100)
         A = X(1)
      DO 10  I=1,N
        IF (X(I).LT.A)  A = X(I)
   10 CONTINUE
      FMIN = A
      RETURN
      END
      FUNCTION  FMAX(N,X)
      DIMENSION  X(100)
         B = X(1)
      DO 11  I=1,N
        IF (X(I).GT.B)  B = X(I)
   11 CONTINUE
      FMAX = B
      RETURN
      END
```

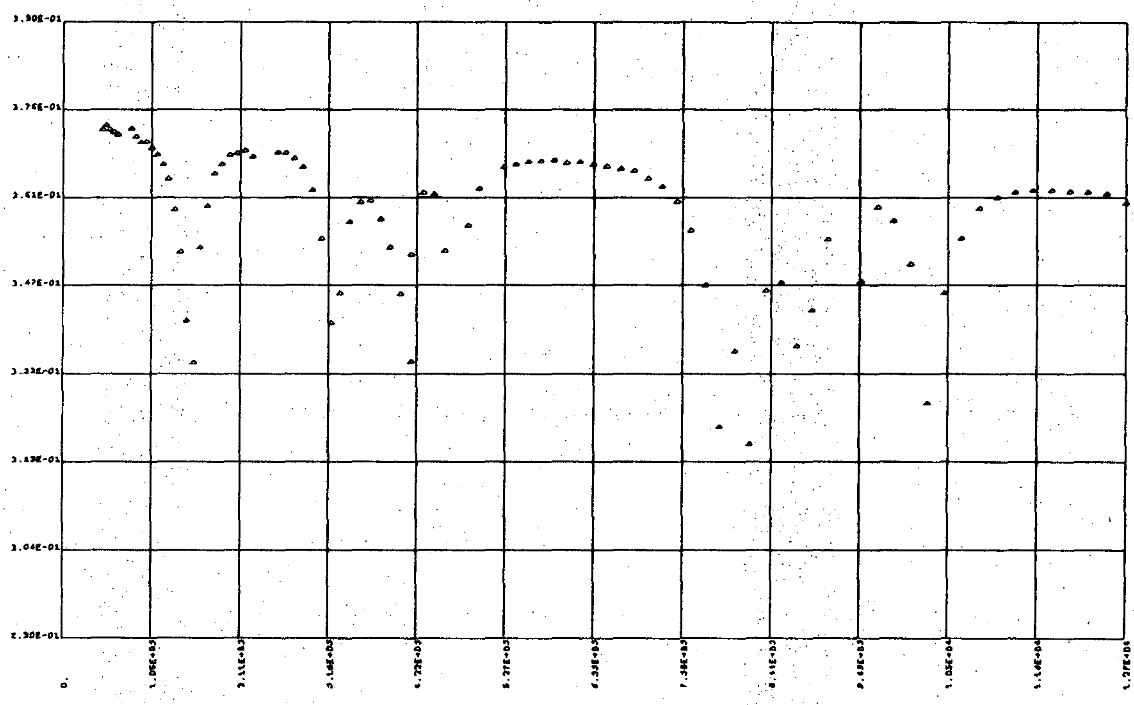
XBL 707-1442

5. <u>TELL 1</u> calculates and plots $\Delta_2F(J)/4(J+\frac{1}{2})$ vs $(J+\frac{1}{2})^2$ (see Eq. 3) for both the upper and lower state levels. Sample plots for the (0,0) band are shown in Figures B-4 and B-5. A sample data deck for the (4,2) band is also given. The first card has the vibrational numbering (4.0, 2.0), the next has the lowest and highest J-numbers for the R- and P-branches up to the first perturbation, then the assigned R and P lines are listed in order, the next set of J-numbers given, etc. The deck is ended by a blank card. Several data decks for different bands can be processed at once. A card with 100. in the first four columns signals the end of the input data.



XBL 706-1178

Fig. B-4. Plot of $\Delta_2''\, F(J)/4(J+\frac{1}{2})$ vs $(J+\frac{1}{2})^2$ for the (0,0) band from program TELL 1. See Eq. 3.



XBL 706-1180

Fig. B-5. Plot of $\Delta_2{}'F(J)/4(J+\frac{1}{2})$ vs $(J+\frac{1}{2})^2$ for the (0,0) band from program TELL 1.

```
      PROGRAM TELL1 (INPUT,OUTPUT,TAPE98,PLOT,TAPE99=PLOT)
      DIMENSION XL(150),XH(150)
      DIMENSION JH(150),HDIFF(150),JL(150),BDIFF(150),P(150),R(150)
      DIMENSION  BVH(150),BVL(150),D2L(150),D2H(150)
      G- 00 157
156   CONTINUE
      PRINT 378, VH,VL
378   FORMAT (1H1*VH,VL= *2F5.1)
101   IH=0
      IL=0
100   READ 1, JRL,JRH,APL,JPH
1     FORMAT (4I5)
      D=JRL-JRH
      IF (D.EQ.0.0) GO TO 155
      DO 400I=1,150
      P(I)=0.0
      R(I)=0.0
400   CONTINUE
      READ 2,(R(I),I=JRL,JRH)
      READ 2, (P(I),I=JPL,JPH)
2     FORMAT (12X,F10.2)
      JS=JRL
      IF (JPL.LT.JRL) JS=JPL
      JE=JRH
      IF(JPH.GT.JRH) JE=JPH
      PRINT 3,(J,P(J),R(J),J=JS,JE)
3     FORMAT (1X,I5,5X,F10.2,5X,F10.2)
401   JO=JPL-2
      IF(JO.LE.1) GO TO 403
      IF(R(JO).EQ.0.0) GO TO 402
      IL=IL+1
      BDIFF(IL)=R(JO)-P(JPL)
      JL(IL)=JPL-1
      XL(IL)=(JL(IL)+.5)**2
      BVL(IL)=BDIFF(IL)/(4.0*(JL(IL)+.5))
      IF(IL.EQ.1)D2L(1)=0.0
      IF (IL.EQ.1 ) GO TO 402
      D2L(IL)=0.0
      JB=JL(IL)-JL(IL-1)
      IF(JB.NE.1) GO TO 402
      D2L(IL)=BDIFF(IL)-BDIFF(IL-1)
402   IF(R(JPL).EQ.0.0) GO TO 403
      IH=IH+1
      HDIFF(IH)=R(JPL)-P(JPL)
      JH(IH)=JPL
      XH(IH)=(JH(IH)+.5)**2
      BVH(IH)=HDIFF(IH)/(4.0*(JH(IH)+.5))
      IF(IH.EQ.1) D2H(1)=0.0
      IF(IH.EQ.1)GO TO 403
      D2H(IH)=0.0
      JB=JH(IH)-JH(IH-1)
      IF(JB.NE.1) GO TO 403
      D2H(IH)=HDIFF(IH)-HDIFF(IH-1)
403   JPL=JPL+1
      IF (JPL.LE.JPH) GO TO 401
      GO TO 100
155   CONTINUE
```

XBL 707-1384

```
      PRINT 181 ,VH,VL
181   FORMAT(1H1*LOWER STATE OF *2F5.1/1X*J*4X*C-DIFF*4X*2ND DIFF*
     1 2X*BV*)
      PRINT 17,(JL(I),BDIFF(I),D2L(I),BVL(I),I=1,IL)
       IN=0
       DO 19 J= 1,IL
       IN=IN+1
       BVL(IN)=BVL(J)
       XL(IN)=XL(J)
19     IF(BVL(J).GT.0.8.OR.BVL(J).LT.0.1) IN=IN-1
       IL=IN
        CALL GRAPH ( XL,BVL,IL)
        CALL LINE (  XL,BVL,IL)
      PRINT 18  ,VH,VL
18    FORMAT(1H1*UPPER STATE OF *2F5.1/1X*J*4X*C-DIFF*4X*2ND DIFF*
     1 2X*BV*)
      PRINT 17,(JH(I),HDIFF(I),D2H(I),BVH(I),I=1,IH)
17    FORMAT (1X,I5,3(5X,F10.5))
      IN=0
       DO 20 J =1,IH
       IN=IN+1
       BVH(IN)=BVH(J)
       XH(IN)=XH(J)
20     IF(BVH(J).GT.0.8.OR.BVH(J).LT.0.1) IN=IN-1
       IH=IN
        CALL GRAPH (  XH,BVH,IH)
        CALL LINE        (XH,BVH,IH)
157    READ 5,VH,VL
5     FORMAT(2F10.2)
       IF (VH.LT.99.0)  GO TO 156
       END
      SUBROUTINE GRAPH (X,Y,NT)
      COMMON/CCPOOL/XL,XH,YL,YH,CXL,CXH,CYL,CYH
      DIMENSION  ROUND(4)
      DIMENSION X(150),Y(150)
      XMIN=FMIN(NT,X) $ XMAX=FMAX(NT,X)
      IB=XMAX+4.0
       IA=0
        XL=IA     $     XH=IB
        NXL=12
        NYL=7
        CXL=100.     $CXH=1300.
      CYL=200.     $    CYH =900.
      NROUND=4
      ROUND(1)=1.0
      ROUND(2)=2.0
      ROUND(3)=2.5
      ROUND(4)=5.0
      CALL LINEUP (Y,NT,ROUND,NROUND,NYL,YL,YH)
      CALL CCGRID (NXL,6HLABELS,NYL)
      CALL CCPLOT (X,Y,NT,6HNOJOIN,8,1)
      CALL CCNEXT
      RETURN
      END
      FUNCTION  FMIN(N,X)
      DIMENSION  X(100)
          A = X(1)
```

XBL 707-1382

```
      DO 10  I=1,N
        IF (X(I).LT.A)  A = X(I)
   10 CONTINUE
      FMIN = A
      RETURN
      END
      FUNCTION  FMAX(N,X)
      DIMENSION  X(100)
          B = X(1)
      DO 11  I=1,N
        IF (X(I).GT.B)  B = X(I)
   11 CONTINUE
      FMAX = B
      RETURN
      END
        SUBROUTINE LINE (X,Y,M)
        DIMENSION X(150),Y(150)
       IA=0
3      CONTINUE
        SX=0.0
        SY=0.0
        SXY=0.0
        SX2=0.0
        DO 1J =1,M
        SX=SX+X(J)
        SY=SY+Y(J)
        SXY=SXY+X(J)*Y(J)
        SX2=SX2+X(J)**2
1       CONTINUE
        R=M
        D=R*SX2-SX**2
        C1= (R*SXY-SX*SY)/D
        C2= (SX2*SY-SX*SXY)/D
        PRINT 2,C1,C2
2      FORMAT (1X*LEAST SQUARES FIT OF LINE C1 X+C2=Y*/10X*C1=*
     1  E12.5/10X*C2=*E12.5)
       IF(IA.GT.0) GO TO 7
       TEST=.015
       J=0
       IA=1+IA
       DO 4I=1,M
       YT=C1*X(I)+C2
       DI=  ABS(YT-Y(I))
       IF(DI.GT.TEST) GO TO 5
       J=J+1
       X(J)=X(I)
       Y(J)=Y(I)
       GO TO 4
5      PRINT 6,X(I),Y(I),DI
6      FORMAT (///40X,3F15.5)
4      CONTINUE
       M=J
       GO TO 3
7        CONTINUE
        RETURN
        END
```

XBL 707-1383

Sample Data Deck for the (4,2) Band

```
4.0        2.0
25    45    24    47
            12884.59
            12883.85
            12882.81
            12881.56
            12880.43
            12879.20
            12877.87
            12876.63
            12875.14
            12873.78
            12872.41
            12870.31
            12868.66
            12867.14
             blank
             blank
             blank
             blank
             blank
            12854.33
            12848.56
            12849.45
            12847.29
            12844.76
            12842.25
            12839.63
            12836.99
            12834.41
            12831.72
            12828.84
            12825.97
            12822.86
            12819.96
            12816.83
            12813.80
            12810.47
            12807.09
            12803.94
            12800.59
            12797.04
            12793.57
            12789.92
            12786.29
            12781.49
            12774.71
46    52    48    54
            12850.86
            12848.56
            12846.12
            12843.64
            12841.05
            12838.58
            12831.61
            12775.07
            12771.14
            12767.13
            12763.17
            12759.05
            12754.92
            12746.49
52    61    54    63
            12838.11
            12833.40
            12830.36
            12827.45
            12825.07
            12821.79
            12818.80
            12814.99
            12810.49
            12803.94
            12752.90
            12746.49
            12742.04
            12737.72
            12733.50
            12728.79
            12724.05
            12718.83
            12712.68
            12704.65
61    69    63    71
            12811.56
            12806.05
            12802.93
            12799.37
            12796.15
            12792.46
            12789.05
            12784.81
            12782.58
            12712.01
            12705.57
            12700.63
            12695.44
            12690.66
            12685.36
            12680.61
            12675.58
            12670.68
blank
```

XBL 707-1378

6. TELL 2 calculates and plots T/4J vs J (see Eq. 4). The same data deck setup used for TELL 1 can be used here. Sample plots are shown in Figs. 8-13.

```
      PROGRAM  TELL2(INPUT,OUTPUT,TAPE98,PLOT,TAPE99=PLOT)
      DIMENSION R(150),P(150),X(150),T(150)
       GO TO 157
156     CONTINUE
       PRINT 378, VH,VL
378    FORMAT (1H1*VH,VL= *2F5.1)
      IT=0
100   READ 1,JRL,JRH,JPL,JPH
1     FORMAT (4I5)
      D=JRL-JRH
      IF (D.EQ.0.0)  GO TO 155
      DO 3I=1,150
      R(I)=0.0
      P(I)=0.0
3     CONTINUE
      READ 2, (R(I),I=JRL,JRH)
      READ 2,(P(I),I=JPL,JPH)
2     FORMAT (12X,F10.2)
      JTEST=JRH+1
      J=JRL+2
4     IF(J.GT.JTEST) GO TO 100
      IF(P(J+1).EQ.0.0.OR.P(J).EQ.0.0.OR.R(J-1).EQ.0.0.OR.R(J-2).EQ.0.)
     1  GO TO 5
      A=J
      IT=IT+1
      T(IT)=(R(J-2)-R(J-1)+P(J)-P(J+1))/(4.0*A)
      X(IT)=A
      PRINT 6,X(IT),T(IT)
6     FORMAT(1X,2F10.5)
        IF(T(IT).GT.0.1.OR.T(IT).LT.0.02) IT=IT-1
5     J=J+1
      GO TO 4
155   CONTINUE
      CALL GRAPH(X,T,IT)
157    READ 25,VH,VL
25     FORMAT  (2F10.2)
       IF (VH.LT.99.0)  GO TO 156
      CALL CCEND
      END
      SUBROUTINE GRAPH (X,Y,NT)
      COMMON/CCPOOL/XL,XH,YL,YH,CXL,CXH,CYL,CYH
      DIMENSION X(150),Y(150)
      XMIN=FMIN(NT,X) $ XMAX=FMAX(NT,X)
       IF(XMAX.LT.100.)GO TO 9
       JA=XMAX/4.0+1.0
       A=JA
       NXL=JA
       XH=JA*4
       CXH=100.+100.*A
       GO TO 10
9      CXH=2600.
       XH=100.
       NXL=25
10     XL=0.0
        NYL=8
        YL=.02
       YH=.1
```

XBL 707-1394

```
      CXL=100.0
      CYL=200.
      CYH=900.
      CALL CCGRID (NXL,6HLABELS,NYL)
      CALL CCPLOT (X,Y,NT,6HNOJOIN,8,1)
      CALL CCNEXT
      RETURN
      END
      FUNCTION  FMIN(N,X)
      DIMENSION  X(100)
          A = X(1)
      DO 10  I=1,N
        IF (X(I).LT.A)  A = X(I)
   10 CONTINUE
      FMIN = A
      RETURN
      END
      FUNCTION  FMAX(N,X)
      DIMENSION  X(100)
          B = X(1)
      DO 11  I=1,N
        IF (X(I).GT.B)  B = X(I)
   11 CONTINUE
      FMAX = B
      RETURN
      END
```

XBL 707-1395

7. ORIGIN calculates and plots $[(R(J-1) + P(J))/2]$ vs J^2 (see Eq. 6) and the left-hand side of Eq. 7 vs J. It uses the same data decks as TELL 1 only the second data card for each band has B_v'' (format 10X, F10.2). Sample plots are given in Figs. B-6 and B-7.

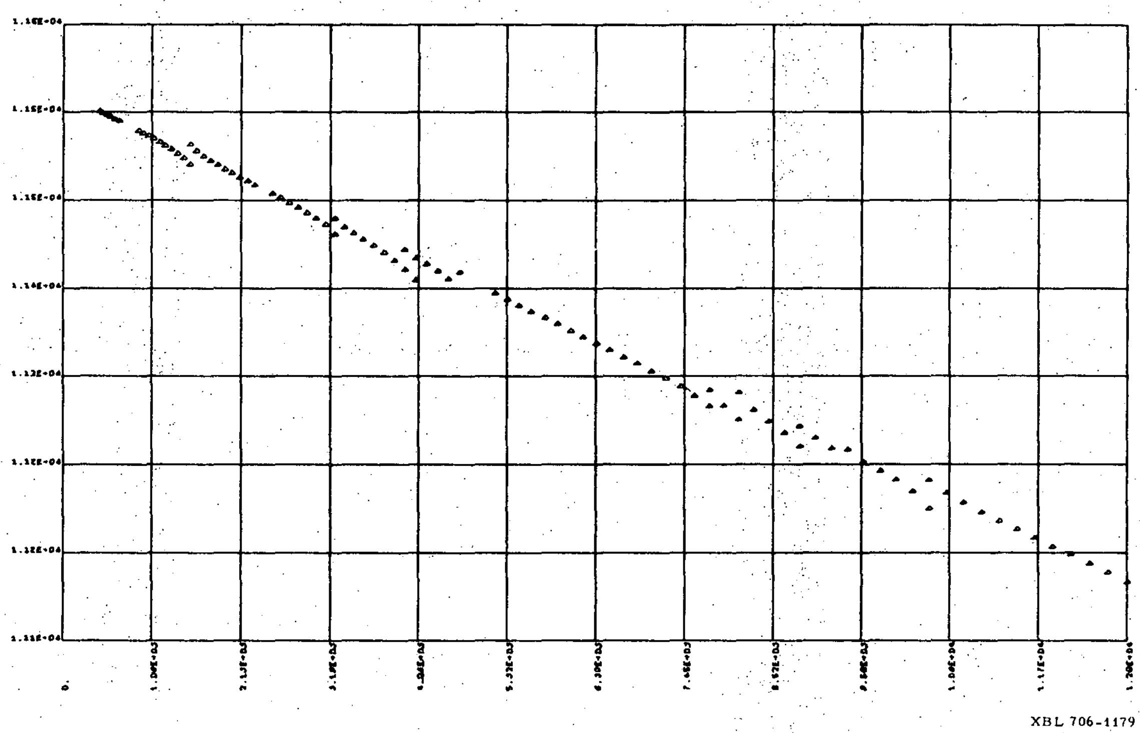
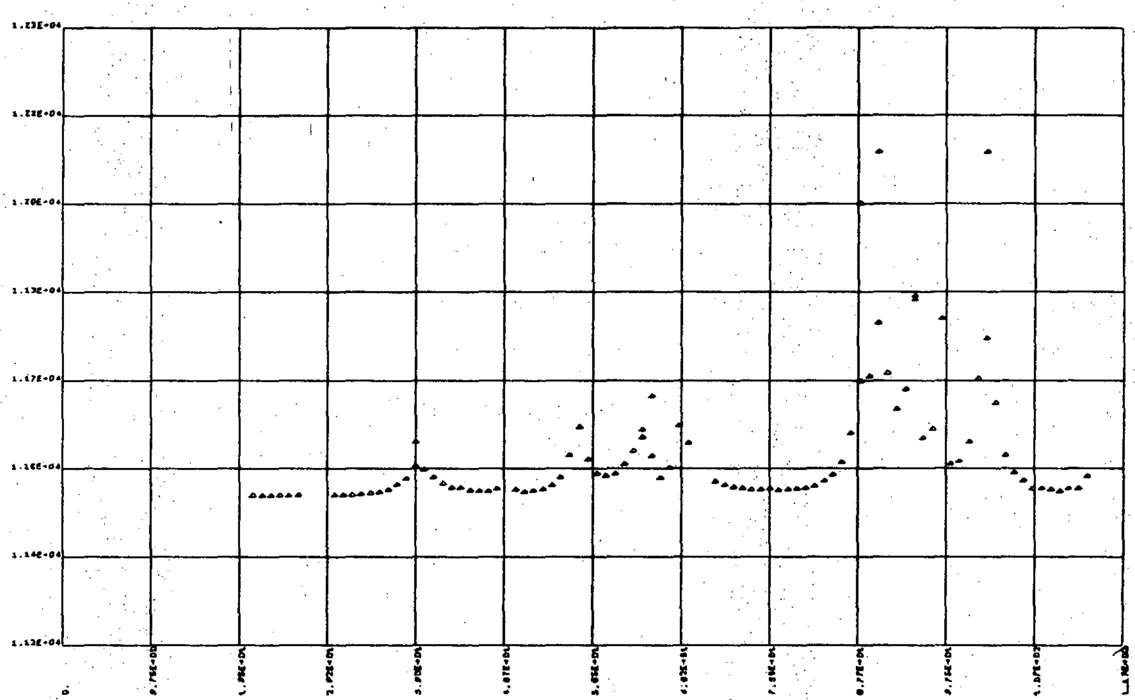


Fig. B-6. Plot of [(R(J-1) + P(J))/2] vs J^2 for the (0,0) band from program ORIGIN. See Eq. 6.



XBL 706-1177

Fig. B-7. Plot of $[B_V'' - \frac{1}{4}\{J(J+1)[P(J)+R(J-2)] - (J-1)[P(J+1) + R(J-1)]]\}$ vs J for the (0,0) band from program ORIGIN. See Eq. 7.

```
      PROGRAM ORIGIN(INPUT,OUTPUT,TAPE98,PLOT,TAPE99=PLOT)
     DIMENSION R(150),P(150),X(150),T(150)
      DIMENSION V1(150),V2(150)
      DIMENSION X1(150)
      GO TO 157
156     C6NTINUE
      PRINT 378,VH,VL
378   FORMAT (1H1*VH,VL=*2F5.1)
      READ 7,BV1,BV2
7     FORMAT(2F10.5)
     IT=0
100  READ 1,JRL,JRH,JPL,JPH
1    FORMAT (4I5)
     D=JRL-JRH
     IF (D.EQ.0.0)  GO TO 155
     DO 3I=1,150
     R(I)=0.0
     P(I)=0.0
3    CONTINUE
     READ 2, (R(I),I=JRL,JRH)
     READ 2,(P(I),I=JPL,JPH)
2    FORMAT (12X,F10.2)
     JTEST=JRH+1
     J=JRL+2
4    IF(J.GT.JTEST) GO TO 100
     IF(P(J+1).EQ.0.0.OR.P(J).EQ.0.0.OR.R(J-1).EQ.0.0.OR.R(J-2).EQ.0.)
    1   GO TO 5
     A=J
     IT=IT+1
      V1(IT)=BV2+.25*((P(J)+R(J-2))*(A+1.0)-(P(J+1)+R(J-1))*(A-1.0))
      V2(IT)=(R(J-1)+P(J))/2.0
      X(IT)=A*A
      X1(IT)=A
      PRINT 8,A,V1(IT),V2(IT),X(IT)
8     FORMAT (1X,4(3X,F10.2))
      IF(V2(IT).GT.15000.0.OR.V2(IT).LT.10000.0)  IT=IT-1
      IF (V1(IT).GT.15000.0.OR.V1(IT).LT.10000.0)  IT=IT-1
5    J=J+1
     GO TO 4
155  CONTINUE
       CALL LINE(X,V2,IT)
      CALL GRAPH(X,V2,IT)
      CALL GRAPH (X1,V1,IT)
157   READ 25,VH,VL
25     FORMAT  (2F10.2  )
      IF (VH.LT.99.0) GO TO 156
     CALL CCEND
     END
     SUBROUTINE GRAPH (X,Y,NT)
     COMMON/CCPOOL/XL,XH,YL,YH,CXL,CXH,CYL,CYH
     DIMENSION  ROUND(4)
     DIMENSION X(150),Y(150)
     XMIN=FMIN(NT,X) $ XMAX=FMAX(NT,X)
     IA=XMIN-4.0
     IB=XMAX+4.0
      XH=IB
      XL=0.0
```

XBL 707-1380

```
      CXL=100.     $CXH=1300.
      NXL=12
      NYL=7
     CYL=200.    $   CYH =900.
      NO=NT+1
      Y(NO)=FMAX(NT,Y) +25.
     NROUND=4
     ROUND(1)=1.0
     ROUND(2)=2.0
     ROUND(3)=2.5
     ROUND(4)=5.0
       CALL LINEUP (Y,NO,ROUND,NROUND,NYL,YL,YH)
      PRINT 1, YL,YH
1     FORMAT (20X*YL,YH=* 2F15.5)
      YWHY=(YH-YL)/7.0
      PRINT 2,YWHY
2     FORMAT (20X*DIVISION=* F15.5)
     CALL CCGRID (NXL,6HLABELS,NYL)
     CALL CCPLOT (X,Y,NT,6HNOJOIN,8,1)
     CALL CCNEXT
     RETURN
     END
     FUNCTION  FMIN(N,X)
     DIMENSION  X(100)
         A = X(1)
     DO 10  I=1,N
       IF (X(I).LT.A)  A = X(I)
  10 CONTINUE
     FMIN = A
     RETURN
     END
     FUNCTION  FMAX(N,X)
     DIMENSION  X(100)
         B = X(1)
     DO 11  I=1,N
       IF (X(I).GT.B)  B = X(I)
  11 CONTINUE
     FMAX = B
     RETURN
     END
       SUBROUTINE LINE (X,Y,M)
       DIMENSION X(150),Y(150)
      IA=0
3     CONTINUE
       SX=0.0
       SY=0.0
       SXY=0.0
       SX2=0.0
       DO 1J =1,M
       SX=SX+X(J)
       SY=SY+Y(J)
       SXY=SXY+X(J)*Y(J)
       SX2=SX2+X(J)**2
1      CONTINUE
       R=M
       D=R*SX2-SX**2
       C1= (R*SXY-SX*SY)/D
```

XBL 707-1379

```
      C2= (SX2*SY-SX*SXY)/D
      PRINT 2,C1,C2
2     FORMAT (1X*LEAST SQUARES FIT OF LINE C1 X+C2=Y*/10X*C1=*
     1 F10.5/10X*C2=*F15.5)
      IF(IA.GT.0) GO TO 7
      TEST=25.
      J=0
      IA=1+IA
      DO 4I=1,M
      YT=C1*X(I)+C2
      DI=  ABS(YT-Y(I))
      IF(DI.GT.TEST) GO TO 5
      J=J+1
      X(J)=X(I)
      Y(J)=Y(I)
      GO TO 4
5     PRINT 6,X(I),Y(I),DI
6     FORMAT (///40X,3F15.5)
4     CONTINUE
      M=J
      GO TO 3
7       CONTINUE
      RETURN
      END
```

XBL 707-1381

8. VIBDIF calculates and plots A/2 vs J^2(see Eq. 10). The input data is two TELL 1-data decks of two bands having the same upper vibrational level.

```
      PROGRAM VIBDIF (HNPUT,OUTPUT,TAPE98,PLOT,TAPE99=PLOT)
      DIMENSION R(150),P(150),V(2,2), X(150),T(2,150),A(150)
      PRINT 1
1     FORMAT (1H1,20X*(R(J-1)-P(J))/2 =V0+(B'-B'')J  2 =T*)
      DO 14I=1,150
      T(1,I)=0.0
      T(2,I)=0.0
14    CONTINUE
      I=1
20    IF(I.GT.2) GO TO 21
      READ 10,V(I,1),V(I,2)
10    FORMAT (8F10.2)
      PRINT 11,V(I,1), V(I,2)
11    FORMAT(//*V',  V''= * 2F10.2)
100   READ 12,JRL,JRH,JPL,JPH
12    FORMAT (4I5)
      D=JRL-JRH
      IF(D.EQ.0.0) GO TO 155
      DO 13 IK=1,150
      R(IK)=0.0
      P(IK)=0.0
13    CONTINUE
      READ 2,(R(IK),IK=JRL,JRH)
      READ 2, (P(IK),IK=JPL,JPH)
2     FORMAT (12X,F10.2)
      J=JPL
6     IF (J.GT.JPH) GO TO 100
4     IF(R(J-1).EQ.0.0.OR.P(J).EQ.0.0) GO TO 5
      T(I,J)=(R(J-1)+P(J))/2.0
      PRINT 15,J,T(I,J)
15    FORMAT (3X,I5,F15.5)
5     J=J+1
      GO TO 6
155   I=I+1
      GO TO 20
21    IT=0
      DO 16 J=1,150
      IF(T(1,J).EQ.0.0.OR.T(2,J).EQ.0.0)  GO TO 16
      IT=IT+1
      IF (V(1,2).GT .V(2,2) )A(IT)=T(2,J)-T(1,J)
      IF(V(1,2).LT.V(2,2))  A(IT)=T(1,J)-T(2,J)
      H=J
      X(IT)=H*H
      PRINT 17,J,X(IT),A(IT)
17    FORMAT (3X,I5,2F15.5)
      IF( A(IT).GT.8000.0.OR.A(IT).LT.-10.)  IT=IT-1
16    CONTINUE
      CALL LINE (X,A,IT,C1,C2)
      CALLGRAPH (X,A,IT)
      CALL CCEND
      END
      SUBROUTINE GRAPH (X,Y,NT)
      COMMON/CCPOOL/XL,XH,YL,YH,CXL,CXH,CYL,CYH
      DIMENSION  ROUND(4)
      DIMENSION X(150),Y(150)
      XMIN=FMIN(NT,X) $ XMAX=FMAX(NT,X)
      IA=0
```

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```
      IB=XMAX+4.0
       XL=IA    $    XH=IB
       CXL=100.    $CXH=1300.
       NXL=12
       NYL=7
      CYL=200.    $   CYH =900.
      NROUND=4
      ROUND(1)=1.0
      ROUND(2)=2.0
      ROUND(3)=2.5
      ROUND(4)=5.0
      CALL LINEUP (Y,NT,ROUND,NROUND,NYL,YL,YH)
        YH=YH+25.
      CALL CCGRID (NXL,6HLABELS,NYL)
      CALL CCPLOT (X,Y,NT,6HNOJOIN,8,1)
      CALL CCNEXT
      RETURN
      END
      FUNCTION  FMIN(N,X)
      DIMENSION  X(100)
          A = X(1)
      DO 10  I=1,N
        IF (X(I).LT.A)  A = X(I)
   10 CONTINUE
      FMIN = A
      RETURN
      END
      FUNCTION  FMAX(N,X)
      DIMENSION  X(100)
          B = X(1)
      DO 11  I=1,N
        IF (X(I).GT.B)  B = X(I)
   11 CONTINUE
      FMAX = B
      RETURN
      END
       SUBROUTINE LINE (X,Y,M,C1,C2)
        DIMENSION X(150),Y(150)
       IA=0
3      CONTINUE
        SX=0.0
        SY=0.0
        SXY=0.0
        SX2=0.0
        DO 1J =1,M
        SX=SX+X(J)
        SY=SY+Y(J)
        SXY=SXY+X(J)*Y(J)
        SX2=SX2+X(J)**2
1       CONTINUE
        R=M
        D=R*SX2-SX**2
        C1= (R*SXY-SX*SY)/D
        C2= (SX2*SY-SX*SXY)/D
        PRINT 2,C1,C2
2      FORMAT (1X*LEAST SQUARES FIT OF LINE C1 X+C2=Y*/10X*C1=*
     1  F10.5/10X*C2=*F15.5)
```

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```
      IF(IA.GT.0) GO TO 7
      TEST=10.
      J=0
      IA=1+IA
      DO 4I=1,M
      YT=C1*X(I)+C2
      DI=  ABS(YT-Y(I))
      IF(DI.GT.TEST) GO TO 5
      J=J+1
      X(J)=X(I)
      Y(J)=Y(I)
      GO TO 4
5     PRINT 6,X(I),Y(I),DI
6     FORMAT (///40X,3F15.5)
4     CONTINUE
      M=J
      GO TO 3
7       CONTINUE
       RETURN
       END
```

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