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Near Infra-Red Bands of Diatomic CaO and SrO

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Running Head: INFRA-RED BANDS OF CaO and SrO

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ABSTRACT

Two band sequences of CaO^{16} and CaO^{18} in the region 0.94 μ to 1.1 μ are shown to be 0-2 and 0-3 tail band sequences of the $A^1\Sigma - X^1\Sigma$ transition of CaO. Band origins and B_v and D_v values are given from a rotational analysis of four bands of the 0-2 sequence. Vibration constants ω_e and $\omega_e x_e$ for the upper and lower states and $\omega_e y_e$ for the lower state are determined from extended sequences of both CaO^{16} and CaO^{18}. Treatment of data on SrO from the literature show a band sequence in the region 1.09 μ to 1.12 μ to be a 0-3 sequence of the $A^1\Sigma - X^1\Sigma$ transition of SrO Vibrational constants ω_e and $\omega_e x_e$ are determined for the lower state. Isotope shifts are given for CaOH band heads.

INTRODUCTION

Bands in the vicinity of 1μ were first observed and assigned to CaO and SrO by Meggers (1). Hultin and Lagerqvist (2) measured CaO bands from 0.7μ to 0.94μ and gave a vibration and rotation analysis. The bands in this region were found to be a $^1\Sigma$-$^1\Sigma$ transition with the 0-0 band at 8652Å. Their analysis showed the upper $^1\Sigma$ state to be highly perturbed by other nearby electronic states. They concluded that the additional bands of CaO reported by Meggers (1) to the red of their system belonged to a different band system. Molecular orbital correlations (3) predict that a $A^1\Sigma$-$^1\Pi$ transition is to be expected to the red of the $A^1\Sigma$-$X^1\Sigma$ transition. Our report presents an experimental investigation and analysis designed to clarify the nature of these bands in the region 0.94μ to 1.1μ.

Almkvist and Lagerqvist (4) examined the spectra of SrO from 0.75μ to 1.1μ. Bands in this region were analyzed as a $^1\Sigma$-$^1\Sigma$ transition with the 0-0 band at 9196Å. Lagerqvist and Selin (5) published further rotational analysis of bands of the 0-2 sequence, and also listed an unassigned band sequence in the region from 1.09μ to 1.12μ. This sequence looks very similar to the two sequences of CaO in the 0.94μ to 1.1μ region and a vibrational analysis similar to the one we have experimentally determined for CaO will show this to be the case.

EXPERIMENTAL

The light source was a reduced pressure arc between Ca metal electrodes. It operated in a helium atmosphere of about 1 cm pressure with small continuous flows of O_2^{16} and O_2^{18} introduced to the arc by means of a hole bored through the center of a Ca metal anode. Flow rates were

such that about 100 ml. of oxygen at 1 atm were consumed per hour of operation.

Low resolution exposures were taken on a 1.5 meter Czerny-Turner spectrometer. The grating is blazed at 1μ and gives approximately 20 Å/mm dispersion in first order. Hyper-sensitized I-M and I-Z emulsions required exposure times from 5 to 15 minutes. Both CaO^{16} and CaO^{18} spectra were photographed at this dispersion. Argon, calcium and oxygen atomic lines were used as wave length standards.

High resolution exposures were taken on a 6.1 meter Czerny-Turner spectrometer. The grating is blazed at 6μ and was used in 6th order with a dispersion of about 1 Å/mm. Four bands were photographed at this dispersion with sensitized I-M emulsion and exposure times of about seven hours. Only CaO^{16} bands were photographed at this dispersion because of the need for approximately 1 liter of oxygen at 1 atm for each exposure.

RESULTS AND DISCUSSION

We have observed the bands previously reported by Meggers (1) and in addition we also have observed weaker bands of each sequence. Tables I and II give our measurements and vibrational assignments for both CaO^{16} and CaO^{18}. Our assignment indicates the bands belong to 0-1, 0-2, and 0-3 tail-band sequences of the $A^1\Sigma$-$X^1\Sigma$ transition for which Hultin and Lagerqvist (2) have previously analyzed the red degraded bands of the 3-0, 2-0, 1-0, 0-0, and 0-1 sequences. The large $\omega_e x_e$ for the lower state results in a reversal of $\Delta G_{v+1/2}$ values between the 0-0 sequence and the 0-v" sequences with v" > 1. However, the order of B_v values does not reverse. This produces the unusual behavior of tail bands with vibrational structure shading to the violet and rotational structure shading to the red,

which obscured the relationship between the tail bands and the previously analyzed bands.

Proof of the assignment can be found in the comparison of calculated and observed isotopic shifts in Table III. The calculated isotopic shifts were obtained by using constants taken from Hultin and Lagerqvist (2). Perturbations cause large differences between calculated and observed isotopic shifts for some bands, but for unperturbed lower members of each sequence the agreement is good. Hultin and Lagerqvist report perturbations of the $A^1\Sigma$ state by six lower states. Of the states predicted by molecular orbital correlations (3) to lie below the $A^1\Sigma$ state, there are only six possible perturbing states $^3\Sigma^-_{0+}$, $^3\Sigma^-_1$, $^1\Pi_1$, $^3\Pi_1$, $^3\Pi_{0^+}$, and $^1\Sigma_{0+}$. Thus every low-lying state must be participating in the perturbation process with resulting complication in analysis of the spectra.

Additional proof of the nature of the bands is furnished by a rotational analysis of the 3-5, 4-6, 5-7, and 6-8 bands. Each of these bands has an upper state in common with bands previously analyzed by Hultin and Lagerqvist and a comparison of their Δ^2F' values and ours shows very good agreement. Band origins and B''_v and D''_v values have been determined from our analysis and are given in Table IV. A complete listing of line measurements used in our rotational analysis can be found in the Ph.D. thesis of R. Hauge (6). The B''_v values in Table IV together with the values from Hultin and Lagerqvist for $v'' = 0$ to 3 yield $B''_v = 0.4444-0.0034\ (v''+\frac{1}{2})$ with an average deviation of 0.0002 cm^{-1}.

The well developed 0-2 and 0-3 sequences provide an opportunity to re-evaluate the vibrational constant ω_e and $\omega_e x_e$ given previously by Hultin and Lagerqvist (2). To do this it is necessary to calculate band

origins from our measured band heads and experimental or extrapolated B_v values. For the lower state, B_v values are experimentally known up to $v'' = 8$, for the upper state up to $v' = 6$ and α_e is well enough determined to allow extrapolation of B_v to $v'' = 13$ and $v' = 11$. D_v values as given by Hultin and Lagerqvist were included in the calculation of origins, but their effect is only noticeable for high v bands with large J values at the head. J is 50 at the head of the 10-13 band and inclusion of D_v values raises the $\Delta G_{12\frac{1}{2}}$ value by 1.4 cm^{-1}. For $\Delta G_{8\frac{1}{2}}$ the effect of D_v is calculated to be 0.1 cm^{-1}. From the band origins we obtain the $\Delta G_{v+\frac{1}{2}}$ listed in Table V.

$\Delta G_{v+\frac{1}{2}}$ (CaO^{18}) values have been adjusted in order to compare them to the $\Delta G_{v+\frac{1}{2}}$ (CaO^{16}) values by converting to $\Delta G_{v+\frac{1}{2}}$ (CaO^{16}) with the isotopic relationship: $\Delta G_{v+\frac{1}{2}}(CaO^{16}) = \Delta G_{v+\frac{1}{2}}(CaO^{18}) + (1-\rho)\,\omega_e - 2(1-\rho^2)\,\omega_e x_e\,(v+1) + (1-\rho^3)\,\omega_e y_e\,(13/4 + 6v + 3v^2)$ where ρ is the square root of the ratio of the reduced masses of CaO^{16} to CaO^{18} and ω_e, $\omega_e x_e$ and $\omega_e y_e$ are vibration constants of CaO^{16} as determined by an initial fit to $\Delta G(CaO^{16})$ values. The $\Delta G''_{v+\frac{1}{2}}$ values for $X^1\Sigma$ agree very well particularly since changing perturbations in the $A^1\Sigma$ state might introduce some error. The effect of changes in perturbations of $A^1\Sigma$ are clearly seen in the lack of agreement for the upper state $\Delta G'_{v+\frac{1}{2}}$ values based on the two isotopic molecules. Our $\Delta G_{v+\frac{1}{2}}$ values and those of Hultin and Lagerqvist (2) are shown plotted against v" in Fig. 1 and 2. Figure 1 shows a line based on the ω_e, and $\omega_e x_e$ values of Hultin and Lagerqvist. The fit is good for low v" numbers but a definite positive deviation of the experimental points is apparent at higher v numbers. A third order constant $\omega_e y_e$ has been determined to account for the deviation such that

$\Delta G_{v+1/2}$ for $X^1\Sigma$ in cm^{-1} is:

$$\Delta G''_{v+1/2} = 723.0 - 10.31v + 0.13\ v^2$$

Figure 2 demonstrates the scatter in $\Delta G'_{v+1/2}$ values for the $A^1\Sigma$ state. One notes, however, that $\Delta G_{v+1/2}$ for v' = 3 and 4 seem particularly well determined since the three independently determined values are in good agreement. From this it would appear that perturbations are not affecting $\Delta G_{v+1/2}$ for these two points and that the best straight line fit of the data should pass through these points. This line is also quite close to what one obtains from a simple least squares fit using data from Hultin and Lagerqvist and both isotopic molecules. It might be noted that an averaging of $\Delta G_{v+1/2}$ values from two isotopic molecules provides an apparent means of removing perturbation effects in the determination of $\Delta G_{v+1/2}$ curves. The equation obtained from a least squares fit to the data of Fig. 2 is

$$\Delta G'_{v+1/2} = 714.7 - 4.23\ v\ cm^{-1}$$

Our molecular constants in cm^{-1} are as follows:

	ω_e	$\omega_e x_e$	$\omega_e y_e$
$X^1\Sigma$	733.4	5.28	~ 0.044
$A^1\Sigma$	718.9	2.11	

The third order constant $\omega_e y_e$ of the $X^1\Sigma$ state is of some interest since, in relation to ω_e and $\omega_e x_e$, it appears to be quite large. In fact its positive value requires additional negative terms of higher power in v in order that $\Delta G_{v+1/2}$ approach zero at high v. This behavior is to be attributed to ionic character as indicated by recent calculations on the

analogous molecules MgO (7) and BeO (8) as well as measurements of the ionic character of SrO and BaO (9). Ionic bonding would introduce a lower order dependence on 1/r of the potential energy and as a result cause a less rapid convergence of $\Delta G_{v+1/2}$ at higher v numbering than one would expect from a Morse potential energy curve. Lagerqvist and Westoo (10) obtain a $\omega_e y_e$ value for BeO of +.0224 cm^{-1}. It should be noted that there is some uncertainty in our $\omega_e y_e$ value since it depends critically on the extrapolated B_v values. However, as mentioned earlier the α_e constants which predict the variation of B_v with v have been determined from a considerable number of experimental values and it is felt that the uncertainty is not large enough compared to the magnitude of the $\Delta G_{v+1/2}$ deviation from linearity.

Lagerqvist and Selin (5) mention the similarity of CaO spectra beyond 9700 Å to the spectra of SrO from 10930 Å to 11135 Å. Since the bands of CaO have been shown to be 0-2 and 0-3 sequences of the $A^1\Sigma$-$X^1\Sigma$ transition, one might expect this to be the case for the unassigned sequence of SrO as well. This can be shown by obtaining the $\Delta G_{v+1/2}$ values from the head measurements of Almkvist and Lagerqvist (4) and using them to calculate the origins of bands of the 0-3 sequence. The extrapolated B_v values of Almkvist and Lagerqvist were used to obtain an estimate of the band head positions. The calculated and measured band heads along with our assignments are given in Table VI. One easily sees how confusion might arise in any attempt at vibrational analysis of these bands since perturbations cause considerable overlapping of the early members of the sequence.

It is possible to obtain values of $\Delta G''_{v+1/2}$ for SrO up to v = 8 by

combining $\Delta G_{v+1/2}$ values of lower v and appropriate band head measurements. Table VII shows the $\Delta G_{v+1/2}$ values obtained in this manner and also $\Delta G_{v+1/2}$ values calculated from an equation obtained from a least squares fit to the above $\Delta G_{v+1/2}$. The equation is

$$\Delta G''_{v+1/2}\ (SrO) = 645.4 - 7.85\ v\ cm^{-1}$$

The vibrational constants for the lower $X^1\Sigma$ state are therefore: ω''_e = 653.2, $\omega''_e x''_e$ = 3.92 cm^{-1}.

The isotope shifts for green and orange systems of CaO and CaOH were also examined. Wet arcs using H_2O and D_2O gave violet degraded bands with doublet heads about 1Å apart in the green in agreement with most of the strong CaOH bands reported by Gaydon (12). Table VIII lists the wavenumbers, wavelengths, and isotope shifts for five of the band heads for which it is believed that the $CaO^{16}H$ and $CaO^{16}D$ features can be matched. The sequence moves to the red and appears very similar to the $^2\Sigma$-$^2\Sigma$ green transition of CaF. With O^{18} containing some water, the $CaO^{16}H$ heads listed in Table VIII shifted to smaller wavenumbers by 1.6 to 1.9 cm^{-1}. $CaO^{16}H$ band heads between 18 001.47 and 17 992.14 cm^{-1} shifted to larger wavenumbers by 1.04 to 1.36 cm^{-1} upon O^{18} substitution. Under high resolution, each of the doublet heads appears to be split again. Only very diffuse band spectra appear in the orange region with the wet arc.

The band structures of both the green and orange regions are quite different when a dry arc is used. Many more bands appear particularly in the orange region. The orange bands did not seem to show any isotope shift when O^{18} was used; it may be necessary to use drier oxygen to eliminate obscuring hydroxide features.

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TABLE I

Band Head Measurements for CaO^{16} ($A^1\Sigma - X^1\Sigma$)
in cm^{-1}, (Å) and vibrational assignment (v'-v")

		10119.8 (9878.9)	0-2	9417.8 (10615.3)	0-3
		10124.2 (9874.6)	1-3	9431.6 (10599.7)	1-4
			2-4		2-5
10848.4 (9215.4)	3-4	10165.0 (9835.0)	3-5	9491.1 (10533.3)	3-6
10867.6 (9199.1)	4-5	10193.6 (9807.4)	4-6	9529.0 (10491.4)	4-7
10891.6 (9178.9)	5-6	10227.0 (9775.4)	5-7	9571.6 (10444.7)	5-8
		10262.8 (9741.3)	6-8	9615.9 (10396.6)	6-9
		10305.9 (9700.5)	7-9	9668.0 (10340.0)	7-10
		10346.8 (9662.2)	8-10	9716.4 (10289.0)	8-11
		10400.2 (9612.6)	9-11	9780.6 (10221.5)	9-12
		10454.8 (9562.4)	10-12	9844.7 (10154.9)	10-13
		10510.0 (9512.1)	11-13		
		10571.5 (9456.8)	12-14		

TABLE II

Band Head Measurements for CaO^{18} ($A^1\Sigma - X^1\Sigma$) in cm^{-1}, (Å) and vibrational assignment (v'-v")

		10176.8 (9823.6)	0-2		0-3
			1-3		1-4
10863.6 (9202.5)	2-3	10197.4 (9803.7)	2-4	9539.5 (10479.8)	2-5
10873.4 (9194.2)	3-4	10215.5 (9786.4)	3-5	9566.1 (10450.7)	3-6
10890.7 (9179.6)	4-5	10241.6 (9761.4)	4-6	9601.4 (10412.3)	4-7
		10272.1 (9732.4)	5-7	9639.9 (10370.7)	5-8
		10308.5 (9698.1)	6-8	9683.9 (10323.6)	6-9
		10342.8 (9665.9)	7-9	9727.6 (10277.2)	7-10
		10386.2 (9625.5)	8-10	9778.6 (10223.6)	8-11
		10429.4 (9585.6)	9-11	9829.6 (10170.0)	9-12
		10479.4 (9539.9)	10-12	9888.9 (10109.6)	10-13
		10530.2 (9493.9)	11-13		
		10587.2 (9442.8)	12-14		

TABLE III

$A^1\Sigma - X^1\Sigma$ Band Head Differences in cm^{-1} for CaO^{16} and CaO^{18}

Band	Calculated $\lambda^{-1}(CaO^{16}) - \lambda^{-1}(CaO^{18})$	Observed $\lambda^{-1}(CaO^{16}) - \lambda^{-1}(CaO^{18})$	$\Delta\lambda^{-1}_{calc.} - \Delta\lambda^{-1}_{obsr.}$
	0-1 Sequence		
0-1	28.5		
1-2	28.0		
2-3	26.9		
3-4	25.2	25.0	+ .2
4-5	23.0	23.1	+ .1
5-6	20.4		
	0-2 Sequence		
0-2	56.7	57.0	- .3
1-3	55.2		
2-4	53.4		
3-5	50.9	50.5	+ .4
4-6	47.2	48.0	- .8
5-7	43.7	45.1	-1.4
6-8	39.8	45.7	-5.9
7-9	35.4	36.9	-1.5
8-10	30.5	39.4	-9.4
9-11	25.1	29.2	-4.1
10-12	19.2	24.6	-5.4
11-13	12.6	20.2	-7.6
12-14	6.4	15.7	-9.3
	0-3 Sequence		
0-3	83.9		
1-4	81.7		
2-5	79.1		
3-6	75.9	75.0	+ .9
4-7	72.4	72.4	0
5-8	68.2	68.3	- .1
6-9	63.4	68.0	-4.6
7-10	58.4	59.6	-1.2
8-11	52.6	62.2	-9.6
9-12	46.4	49.0	-2.6
10-13	39.4	44.2	-4.8

TABLE IV

Band Origins and Rotational Constants for $X^1\Sigma$ of CaO^{16}

v'-v"	origin	v"	B''_v	$D''_v \times 10^6$
3-5	10158.2	5	0.4267	0.90
4-6	10186.2	6	0.4226	0.64
5-7	10216.9	7	0.4187	0.59
6-8	10256.7	8	0.4156	0.71
	cm^{-1}		cm^{-1}	

TABLE V

Values of $\Delta G_{v+1/2}$ (CaO^{16}), cm^{-1}

v	$\Delta G''_{v+1/2}$			$\Delta G'_{v+1/2}$		
		CaO^{16}	CaO^{18*}		CaO^{16}	CaO^{18*}
0	722.5[a]			711.9[a]		
1	712.9[a]			706.8[a]		
2	703.2[a]	702.7		708.1[a]		704.5
3	693.5[b]	693.4	693.4	702.9[a]	703.0	703.8
4		684.2	684.7	698.5[a]	698.6	699.0
5		675.0	675.4	695.4[a]	692.0	697.7
6		665.8	666.0		691.0	686.7
7		657.0	657.6		680.1	686.6
8		649.0	649.8		685.6	678.8
9		640.5	640.4		677.0	678.6
10		634.0	633.2		670.4	671.9
11		624.9	626.4			
12		618.8	619.9			

* Values adjusted to $\Delta G_{v+1/2}$ (CaO^{16}) as outlined in text.

a Values from Hultin and Lagerqvist (2).

b Value from data for C-X system (11).

TABLE VI

Measured* and Calculated Band Heads of SrO ($A^1\Sigma - X^1\Sigma$)

Measured (in cm^{-1})	Vibrational Assignment	Calculated (in cm^{-1})
8959.0	0-3	8959.7
	1-4	8958.6
	2-5	8960.3
8977.5	3-6	8978.5
	4-7	8978.8
8993.6	5-8	8994.9
9015.8	6-9	9017.4
9042.6	7-10	
9073.0	8-11	
9107.8	9-12	
9146.5	10-13	

* Measured values taken from Lagerqvist and Selin.(5).

TABLE VII

$\Delta G''_{v+1/2}$ (SrO^{16}), cm^{-1}

v	Observed	Calculated
0	645.58[a]	645.4
1	637.8[a]	637.6
2	630.1	629.7
3	619.7	621.9
4	615.7	614.0
5	606.0	606.2
6	598.0	598.3
7	591.2	590.5
8	582.3	582.6

[a] Taken from Almkvist and Lagerqvist (4) and Lagerqvist and Selin (5).

TABLE VIII

Wavenumbers and (Wavelengths) of Green System of CaOH

$CaO^{16}H$	$CaO^{16}D$	$\Delta\lambda^{-1}(cm^{-1})$
18021.1	17991.9	-29.2
(5547.5)	(5556.5)	
18025.4	17995.5	-29.9
(5546.2)	(5555.4)	
18037.4	18011.1	-26.3
(5542.5)	(5550.6)	
18041.6	18014.3	-27.3
(5541.2)	(5549.6)	
18046.5	18029.2	-17.3
(5539.7)	(5545.0)	

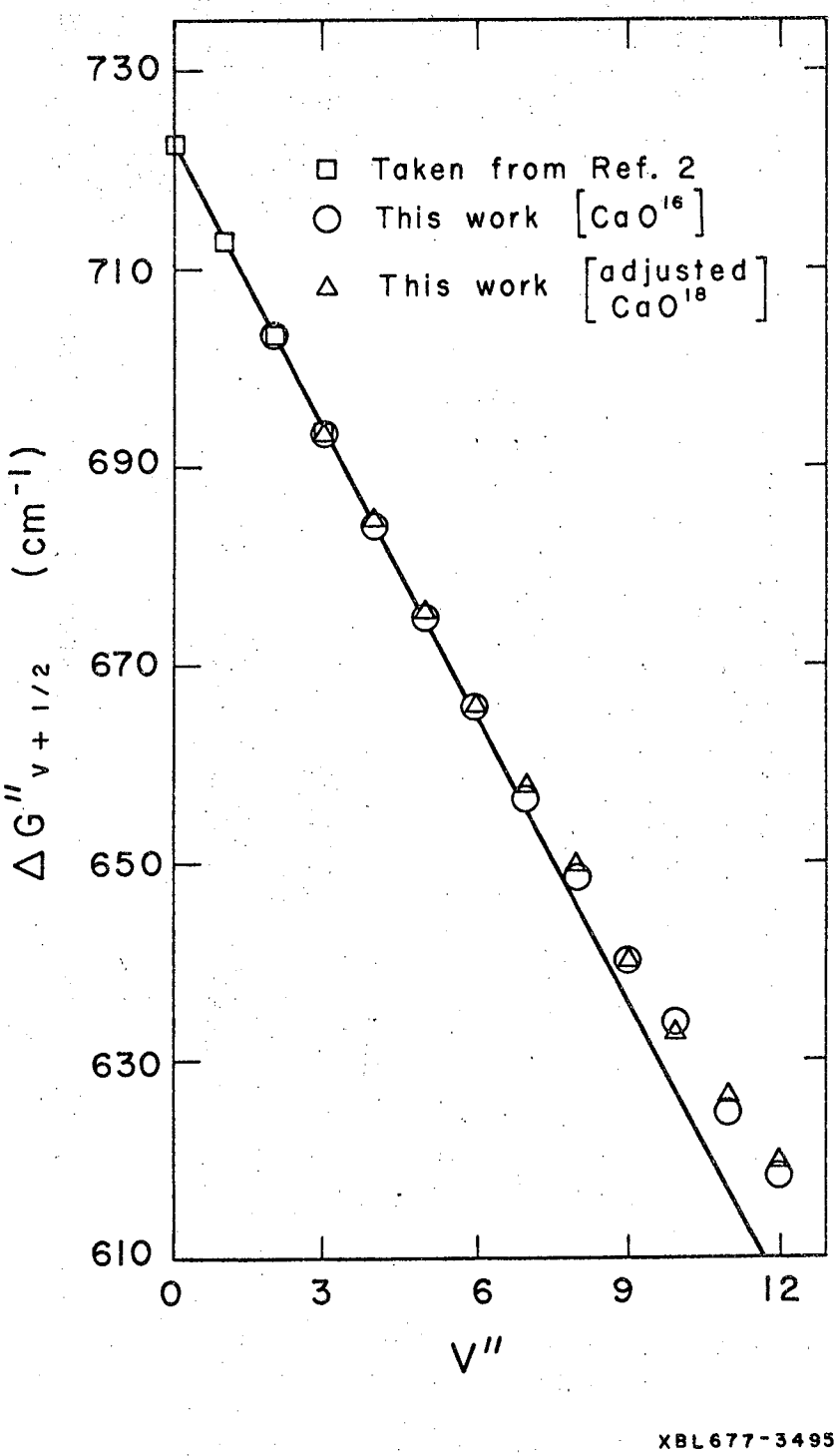

Figure 1. Plot of lower state $\Delta G_{v+\frac{1}{2}}$ values against vibrational number, v".

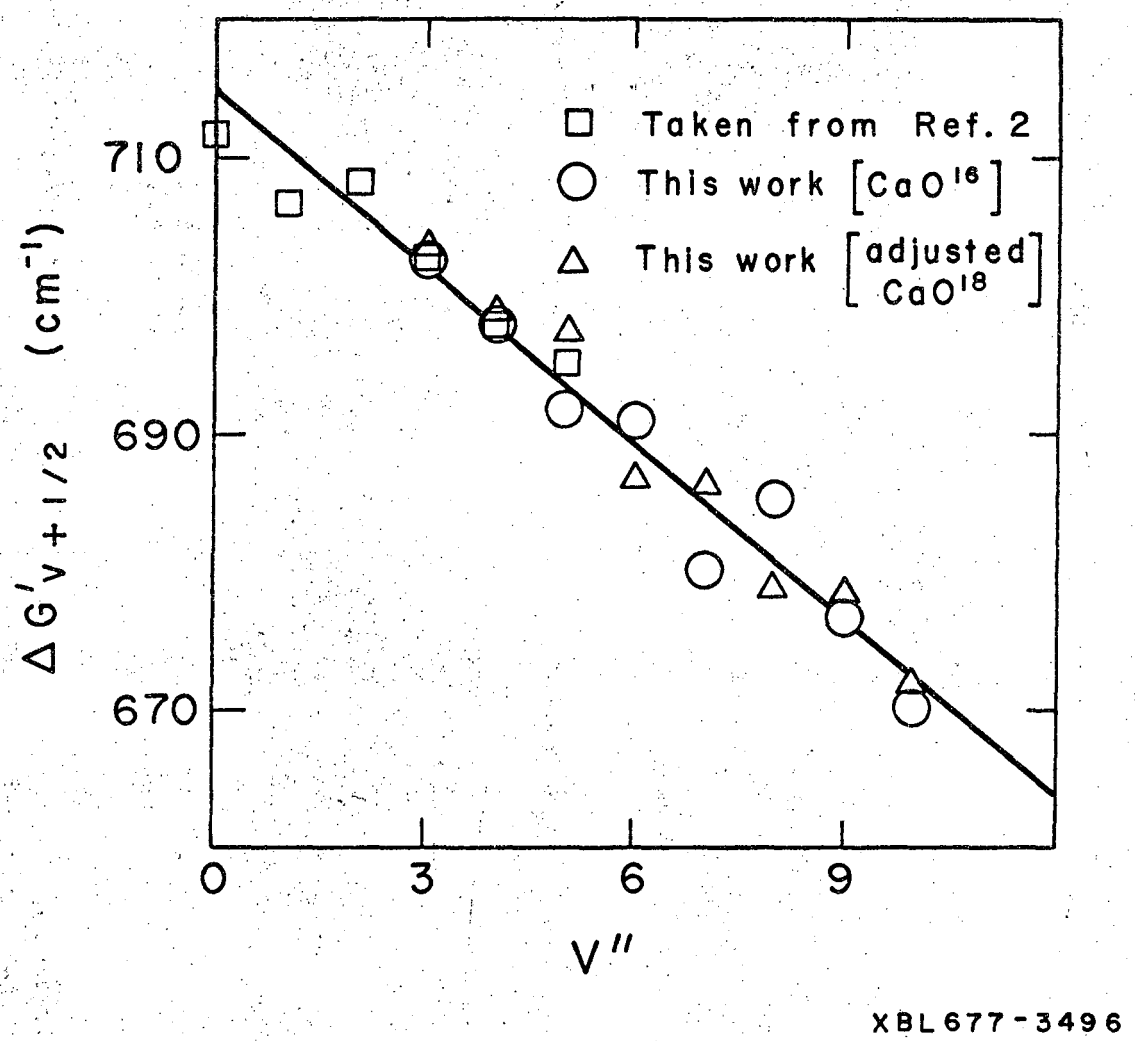

Figure 2. Plot of upper state $\Delta G_{v+\frac{1}{2}}$ values against vibrational number, v'.