Note on Spin Doubling in the Doublet Sigma States of CO^+

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On the photographic plates of the CO_2 spectrum made by S. Mrozowski from the 30-foot, 30,000 lines per inch, Chicago grating, were found pictures of the first negative bands and the comet tail bands of CO^+ in which the $^2\Sigma$ spin splittings were resolved. From the $^2\Sigma\rightarrow{}^2\Sigma$ transition, the absolute differences of the spin doubling coefficients were measured. The absolute values of γ_0'' and γ_1'' for the lowest $^2\Sigma$ state were measured from the $^2\Pi\rightarrow{}^2\Sigma$ transition, and their algebraic signs determined by consideration of relative intensities of branches. Thus the signs and values of the spin doubling coefficients of $^2\Sigma'$ for $v'=0$ to 4, and of $^2\Sigma''$ for $v''=0$ to 7 have been determined.

INTRODUCTION

THE first negative bands of $CO^+(^2\Sigma\rightarrow{}^2\Sigma)$ are well known from the early days of spectroscopy. Their extensive history, which is well related by Kayser,[1] includes no occasion when the spin doublets of these bands were photographed in such a way that they showed measurable resolution. Recently in his comprehensive study of CO_2 on the 30-foot grating at the Ryerson Laboratory, S. Mrozowski has obtained photographs of the first negative bands in the second and third orders, and of the comet tail bands in the second order, in which the $^2\Sigma$ spin splittings were resolved. These plates provided an opportunity to amplify the known experimental data on spin splitting with which to compare predictions of the theory developed by Van Vleck.[2] Such comparisons have already been made for several molecules by Mulliken and Christy[3] who were able to draw conclusions as to the nature of the electronic states involved.

In the present investigation the absolute value of the difference of the spin splitting coefficients for the upper and lower electronic states $|\gamma'-\gamma''|$ was obtained for the $0\rightarrow1$, $0\rightarrow2$, $0\rightarrow3$, $1\rightarrow2$, $1\rightarrow3$, $1\rightarrow4$, $1\rightarrow5$, $2\rightarrow4$, $2\rightarrow5$, $2\rightarrow6$, $3\rightarrow5$, $3\rightarrow6$, $3\rightarrow7$ vibrational bands of the $^2\Sigma\rightarrow{}^2\Sigma$ transition. From an examination of the $5\rightarrow0$, $6\rightarrow0$, $7\rightarrow0$, and $12\rightarrow1$ vibrational transitions of the $^2\Pi\rightarrow{}^2\Sigma$ bands, the absolute values of γ_0'' and γ_1'' were derived. The R_2 and $^RQ_2$, Q_2 and $^QP_2$ branches of the $5\rightarrow0$ and $6\rightarrow0$ bands were identified by consideration of their relative intensities. The sign of γ_0'' then was determined by the sign of $\Delta\nu=R_2-{}^RQ_2=Q_2-{}^QP_2$. With this knowledge, the signs and values of the spin splitting coefficients were determined for the vibrational levels 0 to 4 of the upper $^2\Sigma$ state and for the levels 0 to 7 of the ground $^2\Sigma$ state. γ' was found to increase very slightly with increase in v' while γ'' showed a rather marked increase with v''. Moreover $\gamma'>\gamma''>0$. A similar evaluation of change of spin splitting coefficient with vibrational quantum number was made for the $^2\Sigma\rightarrow{}^2\Sigma$ transition in AlO by M. K. Sen,[4] who found $\gamma'>\gamma''>0$, γ' slowly increasing and γ'' slowly decreasing with increase in v. His paper contains a nice discussion of the theory involved in this analysis, but the accuracy of all constants given therein, especially the B values, is overestimated.

ANALYSIS

The spin splitting in the $^2\Sigma\rightarrow{}^2\Sigma$ bands was originally measured on the third-order plates but this set of data was abandoned in favor of that from the second-order plates, which because of greater intensity showed spin splitting to much higher K values, giving more experimental points and therefore more accurate graphs. For each band the separation of the two components of the spin doublets

$$\Delta\nu_P(K)=P_1(K+\tfrac{1}{2})-P_2(K-\tfrac{1}{2})=(\gamma'-\gamma'')K-\tfrac{1}{2}(\gamma'+\gamma'')$$

$$\Delta\nu_R(K)=R_1(K+\tfrac{1}{2})-R_2(K-\tfrac{1}{2})=(\gamma'-\gamma'')K+\tfrac{1}{2}(3\gamma'-\gamma'')$$

[1] H. Kayser, *Handbuch der Spectroscopie*, Vol. 8.
[2] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).
[3] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).
[4] M. K. Sen, Ind. J. Phys. **11**, 251 (1937).

TABLE I. Data from graphs of doublet splitting.

$\|\gamma'-\gamma''\|$	v'	v''	exp. γ values	Theoretical values for pure precession
0.0180	0	1	$\gamma_0''=+0.0102$	-0.026
0.0159	0	2	$\gamma_1''=+0.0110$	-0.025
0.0153	0	3	$\gamma_2''=+0.0122$	-0.025
			$\gamma_3''=+0.0136$	-0.024
0.0172	1	2	$\gamma_4''=+0.0145$	-0.024
0.0158	1	3	$\gamma_5''=+0.0141$	-0.024
0.0150	1	4	$\gamma_6''=+0.0144$	-0.023
0.0159	1	5	$\gamma_7''=+0.0151$	-0.023
0.0149	2	4	$\gamma_0'=+0.0290$	$+0.022$
0.0153	2	5	$\gamma_1'=+0.0294$	$+0.024$
0.0150	2	6	$\gamma_2'=+0.0294$	$+0.024$
0.0153	3	5	$\gamma_3'=+0.0297$	$+0.024$
0.0153	3	6	$\gamma_4'=+0.0297$	$+0.024$

$\gamma_0''=+0.0102 : \gamma_1''=+0.0109.$

was plotted against m, where for the P branch $\Delta\nu_P(K)$ was plotted against $m=K$, K having the values 1, 2, 3, $\cdots$ and for the R branch, $-\Delta\nu_R(K)$ was plotted against $m=-(K+1)$, K having the values 0, 1, 2, $\cdots$. The result was a single continuous line from whose slope the absolute value of $(\gamma'-\gamma'')$ was determined.

The differences measured in the $^2\Pi\rightarrow{}^2\Sigma$ bands,

$$\Delta\nu=R_2(K)-{}^RQ_2(K)=Q_2(K)-{}^QP_2(K)$$
$$=Q(K)-{}^QR_1(K)=P_1(K)-{}^PQ_1(K),$$

all of which should be given by the equation $\Delta\nu=T_1''(K+\frac{1}{2})-T_2''(K-\frac{1}{2})=\gamma''(K+\frac{1}{2})$, were plotted against $m=K+\frac{1}{2}$. The slopes of these lines determined the absolute values of γ_0'' and γ_1''. The photographs of these bands were made under conditions more favorable to production of CO_2 spectra than CO^+ spectra, and unfortunately the images of the $^2\Pi\rightarrow{}^2\Sigma$ bands were neither intense nor free of other spectra. Consequently the values of γ'' for higher values of v could not be obtained.

The sign of γ_0'' was found by consideration of the sign of $\Delta\nu$ in the $5\rightarrow0$ and $6\rightarrow0$ transitions of the $^2\Pi\rightarrow{}^2\Sigma$ bands. Since $A/B_0=80$ for CO^+, the $^2\Pi$ state approximates Hund's case *a*. As the rotational quantum number increases, however, the spin vector uncouples from the internuclear axis, and there is a transition towards case *b*. The main branches then fulfill the selection rule $\Delta K=\pm1, 0$, because for them $\Delta J=\Delta K$. They remain strong, but the satellite branches suffer decreasing intensity, since for them $\Delta J\neq\Delta K$.[5]

If the lower $^2\Sigma$ level is regular, i.e., $\gamma''>0$, $F(K-\frac{1}{2})$ lies below $F(K+\frac{1}{2})$, Q_2 lies farther to the ultraviolet than does $^QR_2$, and R_2 lies on the ultraviolet side of $^RQ_2$ in the $^2\Pi_{1/2}\rightarrow{}^2\Sigma$ band. In the band $^2\Pi_{3/2}\rightarrow{}^2\Sigma$, $^QR_1$ and $^PQ_1$ must lie on the violet sides of Q_1 and P_1, respectively, if $\gamma''>0$. That is, in the $^2\Pi_{1/2}\rightarrow{}^2\Sigma$ band, the stronger line should lie toward the violet for the Q_2, $^QR_2$ and R_2, $^RQ_2$ branches, and in $^2\Pi_{3/2}\rightarrow{}^2\Sigma$ the stronger line should lie toward the red for the $^QR_1$, Q_1 and $^PQ_1$, P_1 branches. This is true both in the $5\rightarrow0$ and $6\rightarrow0$ transitions of the $^2\Pi\rightarrow{}^2\Sigma$ band; therefore γ_0'' is positive. It is assumed that γ_1'' has the same sign as γ_0''. The $12\rightarrow1$ transition had very low intensity and was so overlapped by other bands that the sign of γ_1'' could not be verified directly from the plates. The data from the graphs of the doublet splitting and the calculated values of the spin splitting coefficients are given in Table I.

The experimental values of the γ's have been obtained by simple algebraic operations with the data. Theoretical values of γ were calculated from Van Vleck's formula

$$\gamma=2AB_v l(l+1)/\nu(\Pi, \Sigma)$$

by assuming a relation of pure precession between the $^2\Sigma$ level considered and the $^2\Pi$ level of the comet tail bands. A is negative for the comet tail $^2\Pi$ level. $\nu(\Pi, \Sigma)$ is obtained by projecting up or down from the $^2\Pi(v')$ level to $^2\Sigma(v'')$ level, and is positive or negative according as the $^2\Pi$ level lies above or below the $^2\Sigma$ level.[3] Hence γ'' is negative and γ' is positive in the theoretical case.

The data indicate a fair degree of likeness to a state of pure precession for the upper $^2\Sigma$ state of CO^+, but very little for the lower $^2\Sigma$ state.

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[5] R. S. Mulliken, Rev. Mod. Phys. **3**, 89 (1931).