Optical–optical double resonance spectroscopy: The $\tilde{G}\ ^2\Pi$ state of CaOH and CaOD

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A large number of polyatomic alkaline earth-containing molecules such as CaOH and CaC_5H_5 are known.[1,2] In general, spectroscopic information is confined to the ground state and the first one or two excited electronic states. The main exceptions are CaOH and CaOD for which the $\tilde{X}\ ^2$, $\tilde{A}\ ^2\Pi$, $\tilde{B}\ ^2\Sigma^+$, $\tilde{C}\ ^2\Delta$, $\tilde{D}\ ^2\Sigma^+$, $\tilde{E}\ ^2\Sigma^+$ and $\tilde{F}$ states have been characterized.[3,4]

Very recently, Pereira and Levy[4] located the $\tilde{D}\ ^2\Sigma^+$, $\tilde{E}\ ^2\Sigma^+$, and the $\tilde{F}$ states of CaOH by pulsed dye laser spectroscopy in a molecular beam. The $\tilde{F}$ state is bent and probably correlates with a $^2\Pi$ state for a linear geometry.

The CaF molecule is isoelectronic with CaOH. Extensive Rydberg series have been measured for CaF by optical–optical double resonance spectroscopy by Field and co-workers.[5] They found that the large dipole moment of the CaF^+ ionic core causes extensive *l*-mixing of the Rydberg orbitals. For a polyatomic molecule such as CaOH additional effects such as Fermi resonance, vibronic coupling and the Renner–Teller effect are possible. It is interesting, therefore, to compare the vibronic states of CaF and CaOH.

Some years ago, we located the $\tilde{G}\ ^2\Pi$ electronic state in CaOH and in CaOD by laser spectroscopy at moderate resolution.[6] The recent work of Pereira and Levy[4] on the $\tilde{D}$, $\tilde{E}$, and $\tilde{F}$ states has inspired us to finally report our preliminary measurements, which slightly extend their observations.

The CaOH and CaOD molecules were made in a Broida oven by the reaction of Ca vapor with H_2O_2 or D_2O_2.[6] The first laser in the optical–optical double resonance experiment was a cw single mode Coherent 699-29 dye laser resonant with a selected rotational line(s) of the 0-0 band of the $\tilde{B}\ ^2\Sigma^+$-$\tilde{X}\ ^2\Sigma^+$ transition. The second laser was a broadband (1 cm^{-1}) linear dye laser (Coherent 599) that was scanned from 610 to 730 nm. The first laser used rhodamine 110 dye while the second laser used either DCM or pyridine 2, all pumped by argon ion lasers. The optical–optical double resonance signal was monitored with a photomultiplier tube and a Corning 7-55 color filter plus a Corion 550 nm short wavelength filter to isolate the UV fluorescence. As the second laser was scanned, the total UV emission was recorded. Wavelength calibration of the second laser was accomplished with a 2/3 meter monochromator.

The optical–optical double resonance spectra revealed the presence of the $\tilde{G}\ ^2\Pi$ electronic state (Fig. 1) at 32 630.2 cm^{-1} for CaOH and 32 628.3 cm^{-1} for CaOD. These values

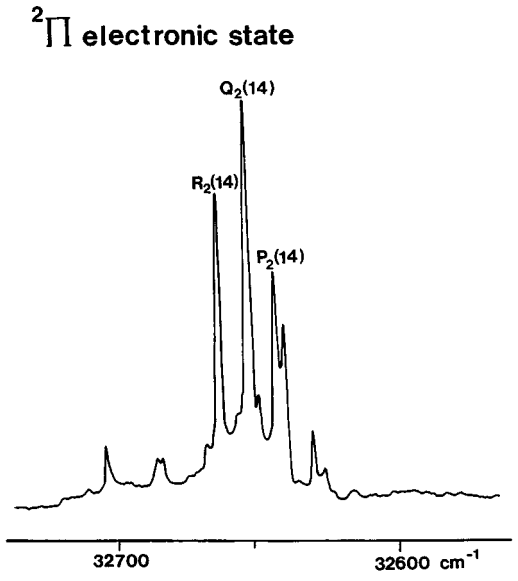

FIG. 1. Spectrum of the $\tilde{G}\ ^2\Pi$-$\tilde{B}\ ^2\Sigma^+$ electronic transition of CaOH taken using optical–optical double resonance spectroscopy. Shown are *R*, *Q*, and *P* lines observed near 32 650 cm^{-1} when the $R_2(13)$ transition of the $\tilde{B}\ ^2\Sigma^+$-$\tilde{X}\ ^2\Sigma^+$ system is optically pumped.

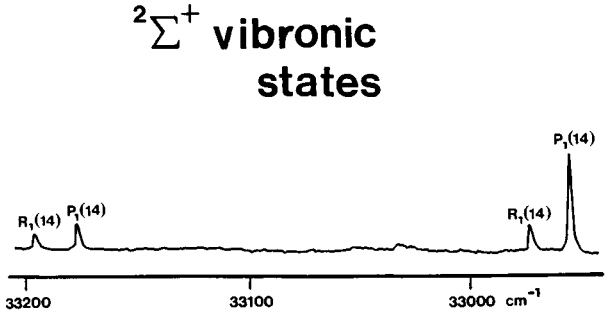

FIG. 2. Optical–optical double resonance spectrum of CaOH connecting to $^2\Sigma^+$ vibronic states. In this section of the spectrum the $R_1(13)$ transition of the $\tilde{B}\ ^2\Sigma^+$-$\tilde{X}\ ^2\Sigma^+$ system was excited in the first step and the higher energy states were scanned with a DCM laser. Two sets of *P* and *R* lines are seen near 33 180 and 32 960 cm^{-1}.

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TABLE I. The term energies and rotational constants for the $\widetilde{G}\ ^2\Pi$ vibronic bands of CaOH and CaOD (in cm^{-1}).

Vibronic symmetry	Vib. assignment	CaOH		CaOH	
		B	T_{v-0}[a]	B	T_{v-0}[a]
$^2\Sigma^+$	?	0.348	33371.2	0.318	33 301.9
$^2\Sigma^+$	?	0.352	33167.3	⋯	⋯
$^2\Sigma^+$	010	0.352	32941.3	0.324	32 895.8
$^2\Pi$	000	0.347	32630.2	0.327	32 628.3

[a]Relative to $v = 0$ of the $\widetilde{X}\ ^2\Sigma^+$ state.

are the 0-0 band origins and the corresponding rotational constants (B values) are 0.347 cm^{-1} and for CaOH and 0.327 cm^{-1} for CaOD. The $\widetilde{G}\ ^2\Pi$ state is close to Hund's case (b) coupling since the $\widetilde{G}\ ^2\Pi_{3/2}$ and $\widetilde{G}\ ^2\Pi_{1/2}$ spin components were not clearly resolved (Fig. 1) using our broadband laser ($\sim$1 cm^{-1}). The simple energy level expression $T_0 + BN(N+1)$ was used for the $\widetilde{G}\ ^2\Pi$ state at this preliminary stage.

In addition to the transition to the $\widetilde{G}\ ^2\Pi$ $v = 0$ vibrational level, three other vibronic bands (Fig. 2, Table I) were seen for CaOH (two for CaOD). The absence of a long progression in the bending mode is consistent with a linear structure for the $\widetilde{G}$ state, by the Franck–Condon principle. These vibronic bands lacked Q-branches and, therefore, have $^2\Sigma^+$ vibronic symmetry like the intermediate $\widetilde{B}\ ^2\Sigma^+$ state. The large OH/OD isotopic shifts and the relatively weak intensity argues against $v = 0$ assignments for these $^2\Sigma^+$ levels. The 32 941.3 cm^{-1} (CaOH) and 32 895.8 cm^{-1} (CaOD) bands can be plausibly assigned as connecting to the 010 $^2\Sigma^+$ vibronic level. The 010 $\widetilde{G}\ ^2\Pi$ state has $^2\Sigma^+$, $^2\Sigma^-$, and $^2\Delta$ vibronic components with the 010 ($^2\Sigma^+$) $\widetilde{G}\ ^2\Pi - 000$ $\widetilde{B}\ ^2\Sigma^+$ forbidden transition occurring weakly because of vibronic coupling. For an allowed electronic transition such as the $\widetilde{G}\ ^2\Pi$-$\widetilde{B}\ ^2\Sigma^+$ transition, the vibrational selection rule[7] for a nonsymmetric vibration such as ν_2 (resulting from the separation of electronic and vibrational motion) is $\Delta v_2 = \pm 2,\ \pm 4,\ \pm 6, \ldots$.

There is precedent for seeing nominally forbidden bands with $\Delta v_2 = 1$ in CaOH,[8] SrOH,[9] and BaOH.[10] This assignments gives $\nu_2 = 311$ cm^{-1} for CaOH and $\nu_2 = 267$ cm^{-1} for CaOD in the $\widetilde{G}\ ^2\Pi$ state compared to the corresponding values of 353 cm^{-1} ($\widetilde{X}\ ^2\Sigma^+$),[8] 312 cm^{-1} ($\widetilde{C}\ ^2\Delta$) for CaOH and 266 cm^{-1} ($\widetilde{X}\ ^2\Sigma^+$), 235 cm^{-1} ($\widetilde{C}\ ^2\Delta$) for CaOD.[3] The other $^2\Sigma^+$ vibronic bands have no obvious assignment. Presumably the combined effects of vibronic coupling, Fermi resonance, and the Renner–Teller effect are playing havoc with the vibrational energy level pattern. Pereira and Levy[4] also experienced some difficulty in making assignments for some of the bands in their spectra. The CaOH molecule is linear, however, in the $\widetilde{G}\ ^2\Pi$ state unlike the bend structure found for the $\widetilde{F}$ state.

The position of the observed electronic energy levels of CaF and CaOH can be compared to each other and with the *ab initio* predictions of Ortiz.[11] (See Table II.) In general, the CaOH states are found at lower energy than the corresponding CaF states. The $\widetilde{G}\ ^2\Pi$ state of CaOH seems to correspond to the $E'\ ^2\Pi$ state of CaF. This correspondence, however, is not perfect since the spin–orbit coupling constant for the $\widetilde{G}\ ^2\Pi$ state of CaOH is less than observed value of 16 cm^{-1} in the $E'\ ^2\Pi$ state of CaF.[12] The electron propagator calculations of Ortiz[11] work very well for CaF and CaOH. Ortiz's calculations have captured the one electron character of the singly-occupied molecular orbital of these monovalent derivatives of Ca. Many interesting questions remain such as why the $\widetilde{F}$ state of CaOH is bent while the nearby $\widetilde{G}\ ^2\Pi$ state is linear. Clearly, more spectroscopic work is necessary at high and low resolution to map out the Rydberg electronic states of CaOH and CaOD.

TABLE II. Electronic states observed and predicted for CaF and CaOH (in cm^{-1}).

State	CaF, calc.[a] T_0	CaF, obs.[b] T_0	State	CaOH, calc.[a] T_0	CaOH, obs. T_0
$F'\ ^2\Sigma$ $(4p)$	36 330	36 125.976	$\widetilde{H}\ ^2\Sigma^+$	31 980	⋯
$E'\ ^2\Pi$ $(5p)$	33 430	34 477.413	$\widetilde{G}\ ^2\Pi$	31 250	32 630.2[c]
$E\ ^2\Sigma^+$ $(4d)$	33 450	34 171.218	$\widetilde{E}\ ^2\Sigma^+$	29 860	29 879[d]
$C\ ^2\Pi$ $(3d)$	31 980	30 215.949	$\widetilde{F}(''\ ^2\Pi'')$	30 010	30 215[d]
$C'\ ^2\Sigma^+$ $(5s)$	28 780	30 158.617	$\widetilde{D}\ ^2\Sigma^+$	26 500	28 153[d]
$B'\ ^2\Delta$ $(3d)$	24 410	21 543.893	$\widetilde{C}\ ^2\Delta$	24 370	21 907.128[e]
$B\ ^2\Sigma^+$ $(3d)$	18 950	18 841.309	$\widetilde{B}\ ^2\Sigma^+$	17 950	18 022.263[f]
$A\ ^2\Pi$ $(4p)$	15 950	16 529.689	$\widetilde{A}\ ^2\Pi$	15 160	15 998.128[g]
$X\ ^2\Sigma^+$ $(4s)$	0.0	0.0	$\widetilde{X}\ ^2\Sigma^+$	0.0	0.0

[a]Reference 11.
[b]Reference 5.
[c]This work.
[d]Reference 4.
[e]Reference 3.
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