Near UV bands of jet-cooled CaO

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Abstract

The electronic spectrum of CaO has been recorded for the 29800-33150 cm⁻¹ energy range. Jet cooling was used to obtain relatively uncongested spectra. Rotationally resolved bands have been assigned to the $C^1\Sigma^+ - X^1\Sigma^+$ and $F^1\Pi - X$ transitions. These data extend the range of vibronic levels characterized for the upper states. Three additional vibronic states were observed as a short progression. One of these levels, which are of 0^+ symmetry, interacts strongly with the $C^1\Sigma^+$, $v'=7$ level. Possible assignments for the perturbing state are considered.

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Introduction

In this study we have examined the electronic spectrum of CaO in the 29800-33150 cm^{-1} energy range. This work was carried out in order to identify vibronic levels that will be suitable for two-photon pulsed-field ionization zero kinetic energy photoelectron characterization of the CaO^+ ion (similar to a previously reported study of BaO^+ [1]). The spectra obtained have provided data for CaO that extend the range of vibronic levels for two known electronically excited states, and revealed a few additional levels that arise from a state of 0^+ symmetry.

The electronic spectrum of CaO is notoriously congested and complex [2-12]. Field and co-workers [12] have developed a very instructive atomic-ions-in-molecules model that provides configurational assignments for the lower energy electronic states. The $X^1\Sigma^+$ ground state is uniquely assigned to the $\text{Ca}^{2+}\text{O}^{2-}$ configuration. The lower energy excited states are then approximated as various configurations of the $\text{Ca}^+ + \text{O}^-$ pair, with an electron localized on Ca and a hole localized on O. All of the previously observed excited electronic states of CaO can be mapped as combinations of molecular states from CaF [13] (which is a model for the electronic structure of the Ca^+ ion) and NaO [14] (which is a model for the electronic structure of the O^- ion). The Ca^+ $X\sigma$, $A\pi$, and $B\sigma$ configurations correspond to the $X^2\Sigma^+$, $A^2\Pi$, and $B^2\Sigma^+$ states of CaF. For O^- the π^{-1} and σ^{-1} configurations correspond to the $X^2\Pi$ and $A^2\Sigma^+$ states of NaO. The configurations of these atomic ions combine to give electronic configurations of the CaO molecule. As an example, the first excited singlet state is $A'^1\Pi$, which arises from the $X\sigma\pi^{-1}$ configuration. There have been several high-level theoretical studies of the electronic states of CaO [15-21], mostly focused on the ground and low-lying excited states. Overall, the electronic structure calculations support the atomic-ions-in-molecules model of Field and co-workers [12].

The present results extend the range of observed vibrational levels for the $C^1\Sigma^+$ and $F^1\Pi$ states. These excited states have been attributed to the $B\sigma\sigma^{-1}$ and $B\sigma\pi^{-1}$ configurations. Data for the $C^1\Sigma^+$ state were obtained by Lagerqvist [6] who observed the $v'=0-3$ levels in emission spectra for the $C^1\Sigma^+-X$ transition. Baldwin and Field [22] characterized the 0-0 origin band of the $F^1\Pi - A'^1\Pi$ transition, which provided the only experimental data available for the $F^1\Pi$ state. Three other vibronic levels were observed, where the rotational structure was consistent with an electronic state of 0^+ symmetry. One of these levels interacts strongly with the $C^1\Sigma^+ v \leq 7$ level.

Experimental

Figure 1 shows the instruments used to record the laser induced fluorescence (LIF) spectrum of CaO. To produce CaO, 1064 nm light from a pulsed Nd:YAG laser (Quanta-Ray, DCR-1A) was focused onto a calcium rod (ESPI Metals, 99.9% pure) to ablate Ca into the gas phase. The calcium rod was continuously rotated and translated using a stepper motor to ensure that a fresh surface of metal was used for each ablation shot. The ablated material was entrained in a pulse of helium carrier gas at ~ 10 atm backing pressure. The He contained a small amount of N₂O ($\sim 0.2\%$) to provide a source of oxygen for production of CaO. The ideal conditions for producing CaO were obtained when the Nd:YAG laser was operated at low power, just above the lasing threshold. The gas pulses were produced using a Parker-Hannifin General Valve (Series 9), with a pulse duration of 500 μ s. After travelling through a short channel (2 mm diameter, ~ 6 mm long) the gas exited the ablation source into a vacuum chamber, forming a supersonic expansion. The vacuum was maintained using a Roots blower (Leybold, RUVAC WSU 251) backed by a rotary vane pump (Leybold, TRIVAC D65B). The background pressure in the chamber was typically < 10 mTorr.

Once the molecules were formed in the supersonic expansion, they were probed using light from a tunable pulsed dye laser (Lambda Physik, FL3002) pumped by a XeCl excimer laser (Lambda Physik, EMG201). The laser was operated at 10 Hz with a nominal pulse duration of 10 ns. To generate tunable UV light, the output of the dye laser was frequency doubled using a BBO crystal (Lambda Physik, FL30). The linewidth of the doubled light was ~ 0.4 cm⁻¹ when the dye laser operated without an intra-cavity etalon, and ~ 0.1 cm⁻¹ when the etalon was used. The fundamental light from the dye laser was directed through an iodine cell for absolute wavenumber calibration using the *B-X* transition. Calibration was performed by comparing the measured iodine spectra to the iodine atlas reported by Salami and Ross [23]. The frequency accuracy of the fundamental light was ~ 0.03 cm⁻¹ without the intra-cavity etalon and ~ 0.01 cm⁻¹ when the etalon was used.

The UV light passed through a short-pass filter (to block the fundamental) and was sent into the vacuum chamber, where the laser light crossed the supersonic expansion ~ 2.5 cm downstream from the nozzle. A two-lens telescope was situated beneath the expansion, perpendicular to both the expansion and the probe laser, to collect fluorescence and focus it onto

a photomultiplier tube (PMT). The signal from the PMT was sent to two boxcar integrators (Stanford Research Systems, SR250), time-gated to integrate over the fluorescence signal and the background signal, respectively. The outputs from the boxcar integrators were sent to an analog processor (Stanford Research Systems, SR235) where the background signal was subtracted from the fluorescence signal. The subtracted signal was then sent to a computer, where it was recorded using a data acquisition card (National Instruments, USB-6210). A custom LabVIEW program was used to control the data acquisition and display. Timing for all of the instruments was maintained using a delay generator (Stanford Research Systems, DG535) that was referenced to the 10 Hz internal frequency standard of the Nd:YAG laser. The optimal delays for observing CaO were to fire the ablation laser $\sim 600 \mu\text{s}$ after opening the pulse valve and then fire the probe laser $24 \mu\text{s}$ after the ablation laser.

To record the spectrum of CaO, the wavelength of the dye laser was stepped sequentially in 0.003 nm steps in the fundamental wavelength (without the intra-cavity etalon) or ~ 0.0005 nm steps in the fundamental wavelength (with the intra-cavity etalon). The boxcar integrators were all set to average 30 shots from the laser. The laser was fixed at each wavelength step for 6 s to allow sufficient time for averaging.

Results and analysis

Figure 2 shows a low-resolution survey scan of the CaO spectrum. An example of two bands recorded at a higher resolution (using the intra-cavity etalon) is shown in Fig. 3. All of the bands observed had rotational structures that were consistent with $^1\Sigma^+ - ^1\Sigma^+$ or $^1\Pi - ^1\Sigma^+$ transitions. The program PGOPHER [24] was used to analyze the rotational structures. The spectra were rotationally cold, but the temperature varied significantly depending on the source conditions. Rotational temperatures ranged from as low as ~ 10 K to as high as ~ 100 K.

Vibrational progressions were readily identified in the survey spectrum (indicated by the symbols $\bullet$, $\dagger$ and $*$ in Fig. 2). The $C-X$ 2-0 and 3-0 bands, previously reported by Lagerqvist [6], were evident in the lower energy part of the spectrum. Compared to the published results, our rotational line positions for these bands were within the experimental uncertainties. Scanning to higher energies it was possible to follow the $C-X$ $\nu' = 0$ progression up to $\nu' = 8$. A few hot-bands

originating from $v''=1$ were also observed. Molecular constants derived from the C - X bands are collected in Table 1. In fitting these bands we fixed the ground state rotational constants at the values reported by Focsa et al. [3] ($B_0''=0.4428$, $B_1''=0.4395$ cm⁻¹). Vibrational constants were obtained by fitting the band origins to the expression

$$T_{v',0} = T_{0,0} + \omega_e'v' - \omega_e x_e'v'(v' + 1) \quad (1)$$

The band origins for the $v'=0$ and 1 levels were taken from ref. [6]. Levels with $v' \geq 7$ were not included in this fit as they were clearly perturbed (see below). Refined vibrational constants for the C state are listed in Table 2. The origins for the 7-0 and 8-0 bands were 26.6 and 18.8 cm⁻¹ above the energies predicted by extrapolation based on the constants of Table 2.

The progression of bands marked by the symbol † in Fig. 2 exhibited the typical rotational structure for a $^1\Pi$ - $^1\Sigma^+$ transition. To assign these features we began by fitting the rotational lines to obtain the band origins. In the first cycle of fitting both the lower and upper state rotational constants were allowed to vary. From these fits it was clear that all of the bands originated from the X , $v''=0$ level. In the second fitting cycle the ground state rotational constant was fixed at the value given by Focsa et al. [3]. Band origins and upper state rotational constants from these fits are listed in Table 3. The lambda doublet splitting for the $^1\Pi$ state did not produce a significant combination defect at the resolution of our measurements. Similarly, the short range of rotational levels observed did not permit the extraction of significant centrifugal distortion constants, with the exception that the fit of the band at 30299.5 cm⁻¹ was improved by including a negative distortion constant of $D'=-1.4(1) \times 10^{-5}$ cm⁻¹. It is likely that this constant was compensating for the effects of a local perturbation.

As there are two known $^1\Pi$ states close enough to the energy range of Fig. 2 to be considered for the upper state assignment (B and F) [22], we examined the possibility that the new bands were part of the B - X or F - X band systems. This was accomplished by fitting Eq. 1 to the band origins. The vibrational numbering was adjusted to obtain $T_{0,0}$ values that were closest to that of the B (25913.0 cm⁻¹) or F (26794.7 cm⁻¹) states. Using the vibrational numbering of Table 3, the extrapolated $T_{0,0}$ value was 26812(2) cm⁻¹, just 18 cm⁻¹ above the established value for the F state. The smallest difference for the B state was -140 cm⁻¹, obtained by increasing the

vibrational numbering of Table 2 by 2 units. This extrapolation procedure was close enough to assign the new bands to the F - X transition. Consequently, a new fit was made with inclusion of the F state $T_{0,0}$ value from the study of Baldwin and Field [22]. The resulting vibrational constants are listed in Table 2. The standard deviation for this fit was 1.0 cm^{-1} , which we consider to be acceptable as several levels are likely to be influenced by local perturbations.

The bands marked with the symbol * in Fig. 2 showed simple P and R branch rotational structure, consistent with a $^1\Sigma^+ - ^1\Sigma^+$ transition. Based on the lower state rotational constants, the three bands above 32000 cm^{-1} originated from $X, v''=0$ while the band at 31757.1 cm^{-1} was from $v''=1$. The higher energy bands appeared to be a short progression, with asymmetric intervals of 442.5 and 475.7 cm^{-1} . This pattern suggests that there is a relatively strong perturbation. Fig. 3 shows the rotational structures of the 32479.5 cm^{-1} band and the nearby C - X 7-0 band. The latter is also strongly perturbed. In addition, the rotational constant for $C, v'=7$ was anomalously small compared to the trend of the rotational constants for the lower energy vibrational levels (c.f., Table 1). The extrapolated energy for the $C, v'=7$ level, 32496.4 cm^{-1} , is very close to the mid-point between the * bands at 32037.0 and 32955.2 cm^{-1} (32496.1 cm^{-1}), making it feasible that the vibronic state at 32479.5 cm^{-1} and the $C, v'=7$ level (Fig. 3) are mutually perturbing. Consequently, these bands were analyzed using a homogeneous perturbation model as implemented by the PGOPHER software. This fit yielded deperturbed values of $T(C)_{7,0}=32496.7(2)$, $B_7'=0.3521(6)$, $T(*)_{x,0}=32496.3(2)$, $B_x'=0.3087(7)$, and a perturbation matrix element of $17.00(1) \text{ cm}^{-1}$.

The $T(*)_{x,0}$ value was consistent with the expectation based on the mid-point of the flanking * bands (just 0.6 cm^{-1} away). However, the deperturbed $C, v'=7$ origin was still 8.9 cm^{-1} above the extrapolated position. This pattern suggests that a third state is involved in the perturbation. To test the viability of this assumption we examined a Hamiltonian matrix of the form,

$$H = \begin{pmatrix} E_0(0^+, v' = x) & m_1 & 0 \\ m_1 & E_0(C, v' = 7) & m_2 \\ 0 & m_2 & E_0(\alpha) \end{pmatrix}$$

where $E_0(C, v'=7)$ is the energy obtained by extrapolation, using the constants from Table 2, $E_0(0^+, v'=x)$ is the energy from the two-state deperturbation model, and $E_0(\alpha)$ is the unperturbed vibronic energy of the third state. The homogeneous perturbation elements are given by m_1 and m_2 , and it is assumed that the direct interaction between 0^+ , $v'=x$ and α is negligible. The eigenvalues of this Hamiltonian reproduce the observed band origins using the parameters $m_1=19.8$, $m_2=13.0$ and $E_0(\alpha)=32469.0 \text{ cm}^{-1}$. The last two parameters are strongly correlated, and therefore somewhat arbitrary. The primary significance of this exercise is that it demonstrates that the band origin shifts can be explained using a three-state model with physically reasonable parameter values.

Next we consider a possible electronic assignment for the * bands. The short progression of these bands runs almost in step with the C - X bands, indicating that the two states have quite similar potential energy curves. Hence, a possible candidate for the electronic assignment is the $C'^1\Sigma^+$ state, derived from the $A\pi\pi'^1$ configuration. Previously, the $v'=0$ and 1 levels of $C'^1\Sigma^+$ were observed by Baldwin and Field [25] via the $C'^1\Sigma^+ - A'^1\Pi$ transition. To test the viability of the assignment we have fitted the term energies ($T(C')_{v',0}$) using the $v'=0$ and 1 values from Baldwin and Field [25], and the present data for $T(*)_{v',0}$ with $v'=n-1$, n , and $n+1$ to Eq.1. The deperturbed origin was used for $v'=n$ and the value for n was treated as a variable. A reasonable fit was achieved for $n=16$ (standard deviation of $\sigma=7.8 \text{ cm}^{-1}$), and the fitting was improved ($\sigma=0.06 \text{ cm}^{-1}$) by including a second anharmonicity constant. The resulting molecular constants were $T(C')_{0,0}=24363.3(1)$, $\omega_e=555.4(2)$, $\omega_{ex_e}=5.48(3)$, $\omega_{ey_e}=0.103(1) \text{ cm}^{-1}$. These values seem reasonable, but there are other viable assignments such as the $g^3\Pi(0^+)$ and $e^3\Sigma^-(0^+)$ states [10]. It is hoped that future studies of the dispersed fluorescence spectra and fluorescence decay lifetimes will shed further light on the upper state of the * bands.

Conclusion

The present work extends the range of levels observed for the C and F states of CaO . While the C - X electronic transition has been observed before, the F - X transition is reported here for the first time. Based on the integer charge model of Baldwin et al. [12], the F - X transition is a formally allowed one-electron excitation.

Vibronic transitions to three new vibronic levels of a 0^+ state were identified in our spectra. The vibrational intervals suggest that the levels have appreciable vibrational excitation, and that state mixing influences the intensity pattern. It is evident that one of these bands interacts strongly with the $C, v \simeq 7$ level. The characteristics of the new state are compatible with assignment to higher vibrational levels of the previously observed $C'^1\Sigma^+$ state[25], but the assignment is uncertain as there are several other 0^+ states expected in this energy region.

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Fig. 1. Apparatus used to record the laser induced fluorescence spectrum of CaO.

Fig. 2. Low-resolution survey scan showing ro-vibronic bands of CaO. The bands marked with X are from CaOH.

Fig. 3. Rotationally resolved scan of the $C^1\Sigma^+ - X, 7-0$ and $0^+ - X, n-0$ bands.

Table 1. Fitted molecular constants for the $C^1\Sigma^+-X^1\Sigma^+$ bands of CaO

v'	$T_{v',0}$	$B_{v'}$
2	29869.8(1)	0.3652(6)
3	30407.2(1)	0.3620(5)
4	30938.2(2)	0.355(1)
5	31461.8(1)	0.3540(8)
6	31977.6(2)	0.349(1)
7*	32513.5(2)	0.3306(7)
8*	33007.5(1)	0.3439(7)

All values are in units of cm^{-1} . The numbers in parentheses indicate the 1σ errors.

*Strongly perturbed bands.

Table 2. Equilibrium electronic and vibrational constants for the $C^1\Sigma^+$ and $F^1\Pi$ states of CaO

	$C^1\Sigma^+$ (this work)*	$C^1\Sigma^+$ [6]	$F^1\Pi$
$T_{0,0}$	28772.7(5)	28772.4	26794.5(11)
ω_e	559.4(4)	560.9	521.3(3)
$\omega_e x_e$	3.61(6)	4.0	2.59(3)
error	0.4	--	1.0

All values are in units of cm^{-1} . The numbers in parentheses indicate the 1σ errors.

*This fit includes the previously reported band centers from Lagerqvist [6] as well as the data reported in this work. The fit only includes the levels from $v=0-6$ because there are significant perturbations for $v=7-8$, as discussed in the text.

Table 3. Fitted molecular constants for the $F^1\Pi-X^1\Sigma^+$ bands of CaO

v'	$T_{v',0}$	$B_{v'}$
6	29815.4(1)	0.3254(5)
7*	30299.5(2)	0.319(1)
8	30777.7(1)	0.3163(7)
9	31252.2(1)	0.3145(7)
10	31722.0(1)	0.3107(4)
11	32186.5(1)	0.3091(4)
12	32646.0(1)	0.3081(4)
13	33101.2(1)	0.3113(4)

All values are in units of cm^{-1} . The numbers in parentheses indicate the 1σ errors.

*The fit for $v=7$ also included a centrifugal distortion constant, $D = -1.44(8) \times 10^{-5}$.

Table 4. Fitted molecular constants for the $0^+-X^1\Sigma^+$ bands of CaO

v'	$T_{v',0}$	$B_{v'}$
n-1	32037.0(2)	0.316(1)
n*	32479.5(2)	0.330(1)
n+1	32955.2(5)	0.313(3)

All values are in units of cm^{-1} . The numbers in parentheses indicate the 1σ errors.

* Strongly perturbed