

Optical-Optical Double-Resonance Spectroscopy of CaF

The $E^2\Sigma^+$ and $E' \ ^2\Pi$ States

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Optical-optical double-resonance (OODR) spectra of CaF are recorded, with reduced Doppler broadening, using two cw, single-mode dye lasers. Molecular constants for $E^2\Sigma^+$ and $E' \ ^2\Pi$ are obtained from rotational analysis of the 0-0 and 1-0 $E^2\Sigma^+ - A^2\Pi$ bands and the 0-0 $E' \ ^2\Pi - A^2\Pi$ band, supplemented by fragmentary observations on the $E' - A$ 0-1 and 1-1 bands:

| | Main parameters | |
|------------------|-----------------|---------------|
| | $E^2\Sigma^+$ | $E' \ ^2\Pi$ |
| T_0 | 34 171.218(2) | 34 477.413(3) |
| $\Delta G_{1/2}$ | 640.912(3) | 668.991(24) |
| B_e | 0.364393(18) | 0.368423(50) |
| α_e | 0.002266(18) | 0.002375(50) |
| $A(0)$ | — | 16.483(4) |

The $E' \ ^2\Pi$ state is observed for the first time. Improved constants for the $A^2\Pi$ state are obtained by fitting all extant rotational and vibrational information for the $E' - A$ and $A - X$ systems. The E and E' states are found to obey the unique perturber rather than the pure precession relationship.

INTRODUCTION

Optical-optical double-resonance (OODR) excitation spectroscopy has proved to be a useful technique for the analysis of levels 3.4-4.5 eV above the ground state in diatomic molecules [for example, (1, 2)]. OODR allows the automatic and unambiguous projection of an assignment of a visible wavelength spectrum into the ultraviolet. This is particularly useful when convenient lasers for the direct uv transition are lacking or when the direct transition is weak. In the case of CaF this allows detection of the $E' \ ^2\Pi$ state which has not been observed previously, probably due to weak oscillator strength of the $E' - X$ transition.

The use of two single-mode, cw dye lasers gives a substantial increase in signal-to-noise and resolution over broadband and/or pulsed dye lasers. Their large power per unit bandwidth and stable operation make single-mode, cw lasers the lasers of choice for analysis of complex spectra. Linewidths are sub-Doppler, even for most lines arising from collision-induced rotational relaxation.

In the present OODR experiments the $A^2\Pi - X^2\Sigma^+$ analyses of Field *et al.* (3) and Nakagawa *et al.* (4) were used to assign the intermediate level populated

TABLE I

CaF 0-0 $E' \ ^2\Pi-A^2\Pi$ Observed and Calculated Line Positions (in cm^{-1})^a

| J | $P_{1e}(J)$ | $P_{1f}(J)$ | $R_{1e}(J)$ | $R_{1f}(J)$ |
|------|---------------|---------------|--------------|--------------|
| 22.5 | | | | 18002.148(1) |
| 23.5 | | | 18001.857(0) | 003.628(3) |
| 24.5 | | | 003.346(3) | 005.147(1) |
| 25.5 | | | 004.869(0) | 006.708(3) |
| 26.5 | | | 006.435(-1) | 008.300(-2) |
| 27.5 | | | 008.041(-3) | 009.938(2) |
| 28.5 | 17967.742(-1) | 17969.682(-1) | 009.693(1) | 011.612(2) |
| 29.5 | 967.977(1) | 969.938(-3) | 011.381(0) | 013.324(-3) |
| 30.5 | 968.250(-1) | 970.240(-1) | 013.110(-2) | 015.069(-3) |
| 31.5 | 968.574(7) | 970.577(-1) | 014.885(0) | 016.859(-1) |
| 32.5 | | 970.956(1) | 016.699(0) | 018.688(1) |
| 33.5 | | | 018.556(1) | |

| J | $P_{12e}(J)$ | $R_{12e}(J)$ |
|------|---------------|--------------|
| 13.5 | 17896.780(-1) | |
| 14.5 | 896.361(-3) | 17917.935(0) |
| 15.5 | 895.971(-4) | |

| J | $P_{2e}(J)$ | $P_{2f}(J)$ | $R_{2e}(J)$ | $R_{2f}(J)$ |
|------|--------------|---------------|--------------|--------------|
| 8.5 | | | 17929.541(2) | 17929.607(3) |
| 9.5 | | | 930.795(2) | 930.880(3) |
| 10.5 | | | 932.098(3) | 932.206(4) |
| 11.5 | | | 933.444(-1) | 933.578(0) |
| 12.5 | | | 934.840(-1) | 935.004(1) |
| 13.5 | | | 936.281(-3) | 936.478(0) |
| 14.5 | 17915.309(2) | | 937.771(-1) | 938.003(2) |
| 15.5 | 915.353(-3) | | 939.300(-5) | 939.574(2) |
| 16.5 | 915.445(-6) | | 940.877(-5) | 941.189(-1) |
| 17.5 | 915.587(-4) | | - | 942.857(1) |
| 18.5 | 915.774(-10) | | - | - |
| 27.5 | | 17920.184(-2) | 961.006(3) | 961.952(-4) |
| 28.5 | 919.965(0) | 920.867(4) | 963.076(1) | 964.101(-2) |
| 29.5 | - | 921.583(1) | 965.185(-1) | 966.291(0) |
| 30.5 | 921.303(6) | 922.345(2) | | |
| 31.5 | 922.025(3) | | | |
| 32.5 | 922.789(1) | | | |

^aBracketed numbers are (observed-calcd.) in 10^{-3}cm^{-1} .

TABLE II

CaF 1-1 $E'^2\Pi$ - $A^2\Pi$ Observed and Calculated Line Positions (in cm^{-1})^a

| J | $P_{2e}(J)$ | $P_{2f}(J)$ | $R_{2e}(J)$ | $R_{2f}(J)$ |
|------|-------------|--------------|--------------|----------------|
| 18.5 | - | 17990.985(1) | - | - |
| 19.5 | - | 991.257(-1) | 18020.622(5) | 16020.996(-13) |
| 20.5 | - | 991.578(1) | 022.369(8) | 022.793(-7) |
| 21.5 | - | 991.947(6) | - | - |

^aNumbers in parentheses are (observed-calc.) in 10^{-3}cm^{-1} .

TABLE III

CaF 0-0 $E^2\Sigma^+$ - $A^2\Pi$ Observed and Calculated Line Positions (in cm^{-1})^a

| J | $P_{12}(J)$ | $Q_2(J)$ | $R_{12}(J)$ |
|------|---------------|--------------|--------------|
| 8.5 | | | 17611.183(6) |
| 9.5 | 17597.980(-2) | 17611.254(0) | 611.845(6) |
| 10.5 | 597.216(-4) | 611.889(0) | 612.536(6) |
| 11.5 | 596.488(0) | 612.550(-2) | 613.238(-10) |
| 12.5 | 595.781(-3) | 613.238(-6) | 614.000(4) |
| 13.5 | 595.103(-5) | 613.965(1) | 614.776(4) |
| 14.5 | 594.457(-5) | 614.713(0) | 615.580(4) |
| 15.5 | 593.846(2) | 615.488(-2) | - |
| 16.5 | 593.263(7) | - | 617.273(2) |
| 17.5 | | 617.128(-2) | 618.160(-1) |
| 18.5 | | 617.991(-2) | 619.081(-1) |
| 19.5 | | 618.884(-1) | |

| J | $P_2(J)$ | $Q_{12}(J)$ |
|------|--------------|--------------|
| 24.5 | | 17607.091(5) |
| 25.5 | | 607.486(-2) |
| 26.5 | | 607.920(-1) |
| 27.5 | | 608.382(-1) |
| 28.5 | 17607.295(6) | 608.871(-4) |
| 29.5 | 607.754(0) | 609.392(-5) |
| 30.5 | 608.255(5) | |

^aNumbers in parentheses are (obs.-calc.) in 10^{-3}cm^{-1} .

TABLE IV

CaF 1-0 $E^2\Sigma^+ - A^2\Pi$ Observed and Calculated Line Positions (in cm^{-1})^a

| J | $P_{12}(J)$ | $Q_2(J)$ | $R_{12}(J)$ |
|------|---------------|--------------|----------------|
| 9.5 | 18238.702(-2) | | |
| 10.5 | 237.897(-1) | | 18253.109(3) |
| 11.5 | 237.117(-1) | 18253.153(1) | 253.772(5) |
| 12.5 | 236.359(-2) | 253.787(-2) | 254.450(-4) |
| 13.5 | 235.628(0) | 254.450(0) | - |
| 14.5 | 234.922(3) | 255.133(-1) | 255.894(-3) |
| 15.5 | 234.234(-1) | 255.835(-7) | 256.659(4) |
| 16.5 | 233.577(2) | 256.576(1) | 257.443(6) |
| 17.5 | 232.945(4) | 257.333(1) | 258.247(4) |
| 18.5 | | 258.114(1) | 259.069(-4) |
| 19.5 | | 258.905(-14) | |
| J | $P_2(J)$ | $Q_{12}(J)$ | $R_2(J)$ |
| 22.5 | | 18246.047(2) | |
| 23.5 | | 246.306(-3) | |
| 24.5 | | 246.573(0) | |
| 25.5 | | 246.851(-11) | |
| 26.5 | 18245.878(6) | - | |
| 27.5 | 246.164(2) | 247.525(9) | 18287.185(-10) |
| 28.5 | 246.482(4) | 247.886(5) | |
| 29.5 | 246.822(2) | 248.268(-4) | |
| 30.5 | 247.200(12) | 248.676(-12) | |
| 31.5 | 247.580(0) | | |

^aNumbers in parentheses are (observed-calc.) in 10^{-3} cm^{-1} .

by the first laser. Scanning the second laser and monitoring the undispersed uv fluorescence allowed us to observe an OODR excitation spectrum which included transitions into the $E^2\Sigma^+$ and $E' \ ^2\Pi$ states. In addition to characterizing these states, the data were used to improve the $A-X$ constants in a combined $E'-A-X$ "direct approach" least-squares fit (5). To obtain a satisfactory fit, the model of (4) had to be changed by the introduction of an A_J constant (centrifugal distortion of the spin-orbit constant) in both $^2\Pi$ states. The simultaneous fit of the X , A , and E' states includes the microwave-optical double-resonance data of Nakagawa *et al.* (4), their optical data, and our more accurate (by a factor of 4), but less extensive, optical data. This kind of global fit minimizes correlations between parameters and improves the physical meaning of constants [for example, (6)].

TABLE V
 Constants for $v = 0$ of X , A , E , and E' States of CaF (in cm^{-1})^a

| | $X^2\Sigma^+$ | $A^2\Pi$ | $E^2\Sigma^+$ ^b | $E'^2\Pi$ |
|------------|------------------------------------|----------------------------|----------------------------|-----------------------------|
| T_0 | 0.0 | 16 529.689(1) | 34 171.218(2) | 34 477.413(3) |
| B_0 | 0.342488(5) | 0.347537(7) | 0.363260(13) | 0.367236(11) |
| D_0 | 4.5×10^{-7} (7) | 4.61×10^{-7} (7) | 4.27×10^{-7} (13) | 4.50×10^{-7} (9) |
| γ_0 | 1.30×10^{-3} ^c | - | 0.05570(8) | - |
| P_0 | | -0.04454(8) | | 0.05304(12) |
| q_0 | | -2.97×10^{-4} (6) | | 7.74×10^{-4} (3) |
| o_0 | | -1.145 ^d | | 0.298 ^d |
| A_0 | | 71.450(1) | | 16.483(4) |
| A_{J0} | | 1.76×10^{-5} (12) | | -6.71×10^{-5} (35) |

^aOne standard deviation error is given in parentheses.

^bAdded for comparison purposes from Table VI.

^cThe X state value of γ_0 was fixed at the MODR value of (4). This value has been confirmed by us at high J using saturation spectroscopy. Since the spin-rotation splitting was often only partly resolved, variation of γ_0 would have been hazardous.

^dFixed at the unique perturber value of $\frac{1}{8}(\frac{A_v}{B_v})_p$.

EXPERIMENTAL DETAILS

CaF was produced by the $\text{Ca} + \text{SF}_6$ reaction in a Broida-type oven system (7). Argon was used as carrier gas and the pressure in the fluorescence region was typically 2 Torr. Only trace amounts of SF_6 ($\ll 1\%$), introduced in a concentric burner arrangement, were required to produce a CaF flame.

The first laser in the OODR excitation scheme, which transferred population from $X^2\Sigma^+$ to a selected $A^2\Pi$ rotation-vibration level, was a Coherent Radiation Model 599-21 dye laser operated with Rhodamine 6G dye. The second laser was another Model 599-21 but with Rhodamine 110 dye. Both dye lasers were excited with 514.5 nm radiation from a single CR-10 Ar^+ laser. Frequency calibration of each dye laser was accomplished using an I_2 reference cell and frequency markers from a 750-MHz free spectral range, half-confocal Fabry-Perot. This allowed line positions to be measured to $\pm 0.004 \text{ cm}^{-1}$ using an I_2 atlas (8).¹

The experimental data were recorded by leaving the first laser fixed at the peak of a selected transition, unambiguously selecting a v' , J' , and parity level of the $A^2\Pi$ state. The exact location of this transition was determined by scanning the first laser and monitoring the total fluorescence with a Hamamatsu R372 photomultiplier through a Ditic 610-nm (10-nm bandpass) interference filter. The $A-X$ transitions were assigned by measuring the lines relative to I_2 and then using a map of calculated line positions based on Nakagawa's constants (4). The second laser was combined with the first using a beam-splitter and the copropagating beams were focused into the oven with a 12-in. focal length

¹ Wavenumbers from the I_2 atlas used here (8) are too large by 0.0056 cm^{-1} [S. Gerstenhorn and P. Luc, *Rev. Phys. Appl.* **14**, 791-794 (1979)]. All CaF lines and band origins should be decreased by this amount.

TABLE VI
CaF $E^2\Sigma^+$ Constants (in cm^{-1})^a

| | $v = 0$ | $v = 1$ |
|------------|-------------------------------|----------------------------|
| T_v | 34171.218(2) | 34812.130(2) |
| B_v | 0.363260(13) | 0.360994(12) |
| D_v | 4.27×10^{-7} (13) | 3.88×10^{-7} (12) |
| γ_v | 0.05570(8) | 0.04921(8) |
| | $\Delta G_{1/2} = 640.912(3)$ | |
| | $a_e = 0.002266(18)$ | |

^aDetermined from E-A fits with $A^2\Pi$ constants fixed at the values of Table V. Zero of energy is $v = 0$ of $X^2\Sigma^+$ state, as in Table V. Uncertainties in parentheses correspond to one standard deviation.

lens. The second laser was scanned and the ultraviolet fluorescence was observed with a Hamamatsu R212 photomultiplier viewing through a Corning 7-54 filter. For each level excited by the first laser, a series of 1-cm^{-1} scans covering as much as 20 cm^{-1} was made with the second laser in order to observe as many collisional satellites as possible. These lines appear because of collisional population of additional rotational levels in the $A^2\Pi$ state. They were assigned simply by counting from the intense principal OODR line. In order to verify the vibrational and electronic assignments for the E and E' states, fluorescence into $A^2\Pi$ was resolved for a few J values with a Spex Model 1802 1-m monochromator.

RESULTS

The unambiguous nature of laser double-resonance spectroscopy is balanced by the disadvantage that a large amount of work is required to generate and especially to measure precise wavenumbers from high-resolution spectra. Since no perturbations were observed, good molecular constants can be derived from a relatively small set of high-quality measurements. Tables I–IV give the line positions observed. The line positions of Table I were combined with 0–0 A–X data of Nakagawa *et al.* (4) in a direct fit of $E' \ ^2\Pi(v = 0) - A^2\Pi(v = 0) - X^2\Pi(v = 0)$. The Hamiltonian used was the standard $^2\Pi - ^2\Sigma$ Hamiltonian (9). In order to obtain an adequate fit it was found necessary to introduce an A_J constant into the $^2\Pi$ states. The constants obtained from the nonlinear least-squares fit are summarized in Table V. The $E^2\Sigma^+$ $v = 0$ and $v = 1$ constants, summarized in Table VI, were obtained by holding the $A^2\Pi$ constants fixed at the values of Table V.

In order to obtain $\Delta G_{1/2}$ values for the X and A states three lines of the 0–1 $E' \ ^2\Pi - A^2\Pi$ band were measured [$P_{2f}(23.5)$ 17330.856, $P_{2f}(24.5)$ 17331.475, $R_{2f}(22.5)$ 17364.718]. Since term values are available from 0–0 and 1–1 A–X bands and the 0–0 $E' - A$ band, one gets $\Delta G_{1/2} = 582.820(30)$ for $X^2\Sigma^+$ and $\Delta G_{1/2} = 588.447(30)$ with the constants of (4) used for the 1–1 A–X band. In addition, a few lines of the 1–1 $E' \ ^2\Pi - A^2\Pi$ band were also observed (Table II) and used in a least-squares fit to give $\Delta G_{1/2} = 668.991(50)$ for $E' \ ^2\Pi$. In this fit only E_1 and B_1 were

TABLE VII
CaF E , A , and X Vibrational Constants (in cm^{-1})^a

| | $X^2\Sigma^+$ | $A^2\Pi$ | $E^2\Sigma^+$ | $E' \ ^2\Pi$ ^b |
|--------------------------|---------------|-------------|---------------|---------------------------|
| T_e | 0 | 16526.75(1) | 34141.77(3) | 34463.60(67) |
| ω_e | 588.87(8) | 594.86(10) | 648.03(7) | 675.49(130) |
| $\omega_e x_e$ | 3.08(4) | 3.26(6) | 3.61(4) | - |
| $\omega_e x_e$ (Pekeris) | 3.14(3) | 3.27(3) | 2.95(2) | 3.25(6) |
| $\omega_e y_e$ | 0.033(4) | 0.039(6) | 0.033(4) | - |

^aUncertainties in parentheses correspond to one standard deviation.

^bAdded for comparison purposes. The Pekeris value of $\omega_e x_e$ used to calculate T_e and ω_e from T_0 and $\Delta G_{1/2}$ is often accurate to $\sim 20\%$. This estimated error propagates into ω_e and T_e .

allowed to vary with the other constants fixed ($A_1 = 16.363$, $p_1 = 0.047$, $q_1 = 6.8 \times 10^{-4}$, $o_1 = 0.263$, $A_J = -6.7 \times 10^{-5}$, and $D_1 = 4.5 \times 10^{-7}$) at values determined mainly by unique perturber relationships. Note that the o parameter is completely correlated with the band origin so its value affects the determined $\Delta G_{1/2}$'s (as well as A_v constants).

These data can be used to determine the vibrational structure of the E , A , and X states more accurately by combination with bandhead data of Fowler (10) and Johnson (11).² [Some small corrections in $A-X$ assignments of (11) are given in Rosen's compilation (12).] The $A-X$ band origins were estimated from P_{21} bandheads using the vibrational dependence of spin-orbit and rotational constants given in (4) and holding the other parameters fixed at $v = 0$ values. A weighted linear least-squares fit resulted in the constants given in Table VII. The vibrational constants of the $E^2\Sigma^+$ state (Table VII) were determined in a similar fashion from P_2 heads of $E-X$ bands (10) but with the X -state vibrational constants fixed at the values determined from the $A-X$ fit. Uncertainties of the band origins determined from bandheads were considered to be about 0.3 cm^{-1} (and weighted proportional to the reciprocal squared uncertainty) while the rotationally analyzed band origins were weighted with the estimated 1σ values.² The fitted values of $\omega_e x_e$ agree reasonably well with estimates based on the Pekeris relationship (13) but the Pekeris value for the $E^2\Sigma^+$ state seems too low. The Pekeris relationship gives a value of $\omega_e x_e = 3.25 \text{ cm}^{-1}$ for the $E' \ ^2\Pi$ state.

DISCUSSION

The values of the constants derived for the X and A states of CaF agree well with those in (4). The X constants agree within quoted standard deviations but many of our A -state constants lie just outside the standard deviations in (4).

² Vibrational constants of the CaF $X^2\Sigma^+$ state have been redetermined from band origin data alone [M. Dulick, P. Bernath, and R. W. Field, *Canad. J. Phys.* **58**, 703-712 (1980)]. Agreement with those constants is poor, presumably because the band head data (11) are less accurate than 0.3 cm^{-1} . The 1σ uncertainties listed in Table VII should be increased by a factor of 4 for the X , A , and E states.

Our introduction of A_J [note, $A_J(14) = A_D/2(9)$] is responsible for this difference. Our value of A_J is a factor of 6 larger than the value of A_J computed using the formula in (14). This is not too surprising because our A_J is, to some extent, phenomenological since it has absorbed various constants with similar matrix elements such as γ_{II} .

The electronic states of CaF are interesting because many of the transitions can be interpreted in terms of a simple hydrogenic, one-electron picture. CaF behaves like Ca^+F^- with the single nonbonding Ca^+ valence electron responsible for all observed electronic transitions. For instance, the $A^2\Pi$ and $B^2\Sigma^+$ states seem to be part of a $4p$ complex and, hence, obey Van Vleck's pure precession relations (15) with $l = 1$. For the E and E' states a value of $l = 1$ would suggest $\gamma_0 = p_0 = 0.075$. This value is about 40% too large; yet $\gamma_0 \approx p_0$. Consequently, these two states form a unique perturber pair (5) but with l no longer a good quantum number. Using the complete summation definitions of γ_0^{Σ} , p_0^{Π} , and q_0^{Π} (5) but using only one pair of electronic states gives $\langle E^2\Sigma^+ | l_+ | E' \ ^2\Pi \rangle = 1.220$, 1.191, and 0.961 from γ_0^{Σ} , p_0^{Π} , and q_0^{Π} , respectively. The radial dependence of $A(R)$ has also been neglected but it is unimportant at this level of accuracy.

The change in ω_e from the ground-state value of 588.87 cm^{-1} to 648.03 cm^{-1} in the E state and 675.49 cm^{-1} in the E' state indicates that the nonbonding valence electron is actually slightly antibonding. The R_e value changes from 1.95165 \AA in the X state to 1.89544 \AA in the E state and 1.88505 \AA in the E' state. These ω_e and R_e values confirm the expectation that the CaF^+ species is more tightly bound than CaF since (Rydberg-like) highly excited CaF states would resemble the ion.

There is some evidence that the $E' \ ^2\Pi - X^2\Sigma^+$ transition dipole moment is small. The transition was not observed in absorption by Fowler (10) although he observed the $E^2\Sigma^+ - X^2\Sigma^+$ transition (which he described as very weak). He did observe some extra features in this region but assigned them to impurity bands. In addition, we were never able to record rotationally resolved uv emission, which suggests that this emission cannot compete with other radiative channels. The $E' - A$ and $E' - B$ transitions could be observed easily in fluorescence and confirm the vibrational assignment of the E' state. This displays a useful feature of OODR spectroscopy. A weak direct transition in the ultraviolet region of the spectrum can be observed via two strong transitions both in the visible region.

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