

LIFETIME MEASUREMENTS OF $\text{CaCl}^*(A^2\Pi)$ IN A MOLECULAR BEAM

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An effusive thermal molecular beam of CaCl was produced vapourizing a mixture of Ca and CaCl₂ within a crucible with subsequent expansion into vacuum. Lifetimes of $\text{CaCl}^*(A^2\Pi)$ in its two lowest vibrational levels were measured under collision-free conditions using laser-induced fluorescence, and values around 33 ns are found; these are discussed with respect to other available data.

INTRODUCTION

The alkaline earth monohalides are an interesting class of molecules which have been subject to extensive experimental and theoretical investigations over the years. The lowest-lying electronic states exhibit the remarkable feature that their equilibrium separation and their vibrational frequencies are nearly the same as in the ground state. The behaviour of the molecules, revealed in their electronic spectra, can be characterized by the promotion of a non-bonding electron in a molecular orbital, centered mostly on the metal atom, to another excited non-bonding orbital, centered on the metal atom as well. Using this model one should be able to gain insight into the nature of bonding of the alkaline earth monohalides when measuring radiative lifetimes and transition moments, and the validity or the limitation of the model may be exposed by the degree of agreement between experiment and expectation.

Of particular importance in the investigations of the alkaline earth monohalides has been CaCl, a molecule of considerable astrophysical interest having been observed in the spectra of cool intermediate stars (see e.g. reference¹); knowledge of the transition moment, which can be deduced from the measurement of radiative lifetimes, can be important aid to determine the concentrations of CaCl.

Very few experimental investigations of lifetimes of the alkaline earth monohalides have been carried out to date, the earliest being undertaken by Capelle *et al.*² for BaCl and BaBr. A quite extensive survey for selected monohalides of Ca, Sr and

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Ba in their lowest electronic excitation states has been performed by Dagdigian *et al.*³ For CaCl there are only three measurements reported since then, namely for the $B^2\Sigma^+$ state,⁴ the $D^2\Sigma^+$ state⁵ and the $E^2\Sigma^+$ state,⁶ while for the lowest-lying excited state allowed for dipole transitions, $A^2\Pi$, no experimental investigation had been undertaken, to our knowledge, until this year.

Two theoretical papers^{7,8} give estimates for the radiative lifetimes of CaCl(*A*) and CaCl(*B*) and predict a variation of lifetimes with increasing vibrational quantum number. The *B*-state has been investigated experimentally, for a few vibrational levels, by Dagdigian⁴ but no such experiments have been performed for the *A*-state.

This situation has motivated us to undertake the present experimental studies which are performed in a collision-free environment, a condition not necessarily fulfilled in the previous investigations, and we report values for the lifetimes of the two lowest vibrational levels of CaCl(*A*), separately for the two substates $A_1^2\Pi_{1/2}$ and $A_2^2\Pi_{3/2}$. It should be mentioned that in parallel to our measurements also Corbett⁹ and Berg *et al.*⁵ determined lifetimes for the lowest vibrational level, $v' = 0$, in CaCl(A_2) and CaCl(A_1), respectively; however, their measurements were not performed under collision-free conditions.

EXPERIMENT

The molecular beam apparatus used in this investigation is similar to the system described already elsewhere^{10,11} but was modified to perform LIF measurements. Therefore, only a brief description will be given here.

A molecular beam of calcium monochloride, CaCl, was produced by vapourizing a mixture of calcium metal, Ca, and calcium dichloride, CaCl₂, contained within a heated stainless steel crucible, typically at a temperature of 1350 K.¹² The product CaCl is formed in the reaction $\text{Ca} + \text{CaCl}_2 \rightarrow 2 \cdot \text{CaCl}$. The molecular beam was collimated to a diameter of 3 mm. The pressure within the vacuum chamber is well below 10^{-5} mbar so that all experiments are performed under collision free conditions.

The number density of CaCl within the beam was monitored measuring its LIF spectrum using a N₂ laser-pumped dye laser (Lambda Physik, N₂ laser K600 plus dye laser FL2000) with the bandwidth adjusted to ≈ 0.07 nm; this has been determined by scanning the line profile of selected transitions in a Na/Ne hollow-cathode lamp using opto-galvanic detection. The reason for the choice of such a broad bandwidth will be given further below. The laser system was typically operated at a pulse repetition rate of 25 Hz, providing pulses of tunable light with an energy of ≈ 50 μJ and a duration of ≤ 4 ns. The wavelength range 600–630 nm of rhodamine 6G covers the excitation of CaCl in the $\Delta v = 0, +1$ sequences of the transition $X^2\Sigma \rightarrow A^2\Pi_{1/2}, ^2\Pi_{3/2}$.

The excitation zone of 2 mm diameter and 3 mm length was observed through a field lens telescope and imaged onto the photocathode of a photomultiplier (RCA C31034-02). The signal from the photomultiplier, after amplification, is sampled by a boxcar averager (Stanford Research Systems SR250) with an integration gate width

of 2.5 ns for the lifetime measurements and 50 ns for the recording of LIF spectra. The instrument is interfaced to a microcomputer for data storage and analysis; the same computer also controls the wavelength setting of the tunable dye laser.

TIME-RESOLVED FLUORESCENCE DECONVOLUTION METHOD

To extract lifetimes from the fluorescence decay signals a deconvolution method was used to account for the time duration of the laser pulse ($T \approx 4$ ns) and for the time response of the electronics (RC). A full description of the procedure can be found elsewhere (Verdasco, 1989), and therefore only a brief account is given here.

The unperturbed fluorescence decay after excitation, given by

$$I(t) = (1/\tau) \cdot \exp(-t/\tau) \quad (1)$$

with τ being the radiative lifetime, can be distorted by both the electronic response function and the laser pulse duration, and the measured fluorescence signal $F(t)$ has to be written as

$$F(t) = (1/RC) \int \exp(-(t-t')/RC) \cdot G(t') dt' \quad (2)$$

where $G(t')$ is the (ideal) time dependent signal for zero electronic time response. This function is related to the fluorescence signal by the duration of the laser pulse and can be written as

$$G(t') = \int_{-\infty}^{\infty} I(\lambda) \cdot A(\lambda - t') d\lambda \quad (3)$$

where the "gate" function A has been chosen to follow a Gaussian distribution

$$A(\lambda - t') = (1/\sqrt{2\pi}) \int_{-\infty}^{\infty} (1/T) \cdot \exp(-(\lambda - t')^2/2T^2) d\lambda \quad (4)$$

with T being the duration of the laser pulse. The approximation of the laser pulse by a Gaussian function is reasonably accurate in the case of our specific laser system, but for other lasers a more appropriate distribution function may have to be chosen.

As a first test we calibrated the response of our detection system, without any CaCl beam present, using as an input signal a laser light pulse which, in comparison to usual experimental conditions, was attenuated by a few orders of magnitude to avoid saturation. In this case the convolution integral in Eq. (2) reduces to

$$F(t) = \int \exp(-(t-t')/RC) \cdot A(t') dt' \quad (5)$$

Using this procedure a value of 16 ± 1 ns was obtained for the RC response. Taking this value of the response, together with the laser pulse width $T = 4$ ns, the

experimental data were fitted using Eq. (2). It should be pointed out that in another investigation¹² excellent agreement has been found between reported lifetimes and those determined by the above procedure.

RESULTS

LIF Spectra

A typical LIF spectrum obtained under the conditions described in the experimental section is shown in Figure 1a; this is compared to a simulated spectrum displayed in Figure 1b (it has been multiplied with the spectral response of the dye laser and the photomultiplier given in Figure 1c).

The simulation comprises a spectrum for thermal population distributions related to $T_{\text{vib}} = T_{\text{rot}} = 1150$ K which is lower than the temperature of the crucible

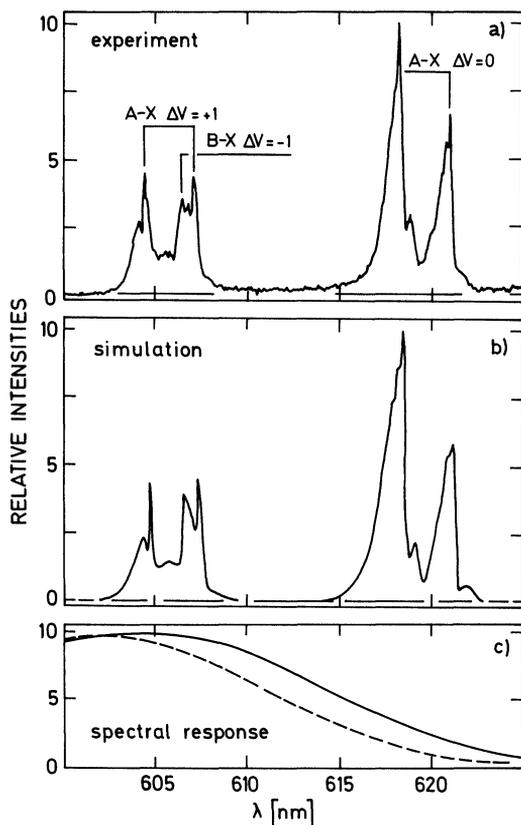


Figure 1 Spectral features of CaCl, (a) typical LIF spectrum of CaCl formed in the Ca + CaCl₂ oven reaction, (b) simulated fluorescence spectrum for $T_{\text{vib}} = T_{\text{rot}} = 1150$ K, (c) spectral response for the dye laser (—) and the dye laser plus detection system (- - -).

Table 1 Spectroscopic constants (in cm⁻¹) for the X²Σ⁺, A²Π and B²Π states of Ca³⁵Cl (adapted from Ernst *et al.*¹³ and Telle¹⁴)

	X ² Σ ⁺	A ₁ ² Π _{1/2}	A ₂ ² Π _{3/2}	B ² Σ ⁺
T _e	0.0	16,096.79	16,167.47	16,856.684
ω _e	370.201	372.89	372.71	367.196
ω _e x _e	1.3732	1.458	1.465	1.524
ω _e y _e	0.0093	0.0106	0.105	0.0086
B _e	0.1522325	0.153773	0.154446	0.154694
α _e	7.998 · 10 ⁻⁴	8.439 · 10 ⁻⁴	8.554 · 10 ⁻⁴	8.839 · 10 ⁻⁴
D _e	1.0297 · 10 ⁻⁷	1.0455 · 10 ⁻⁷	1.0608 · 10 ⁻⁷	1.0983 · 10 ⁻⁷
β _e	6.234 · 10 ⁻¹¹	7.565 · 10 ⁻¹¹	7.784 · 10 ⁻¹¹	1.424 · 10 ⁻¹⁰
τ _e	1.38 · 10 ⁻³	-0.0642		-0.652
p _e —		-2.1 · 10 ⁻⁴		—
q _e				—

(≈1400 K); this reflects the cooling effect in the molecular state distributions due to supersonic expansion. The cooling ratio is in agreement with our measurements for the velocity distribution for Ca*(³P) for which we found a peak velocity of 1.13 · 10⁵ cm/s and a FWHM of ≈18%. The agreement in shape between the experimental and simulated spectra suggests that the state distribution within the CaCl beam is indeed nearly thermal.

The simulation utilizes the spectroscopic constants summarized in *Table 1*; these constants represent hybrid values adapted from high resolution investigations for the three lowest vibrational levels¹³ and values for higher vibrational levels gained from exothermic reaction spectra.¹⁴

For some runs a low-voltage discharge of 20 V, sustaining a current of ≈ 0.5 A, was applied between the collimator and the nozzle thus producing excited Ca* atoms in their metastable ³P and ¹D states. In this way the intensity of the LIF signal is increased by a factor of two whereas the overall shape of the spectrum remains nearly unaffected. Essentially, the increase in intensity reflects a higher concentration of CaCl. This is thought to be due to an increase in photo and electron impact fragmentation of CaCl₂ rather than an increase due to the excited state reaction Ca* + CaCl₂ → 2 · CaCl which is unlikely because of the low-density conditions in these experiments. Thus the presence of Ca* does not result in the population of high-lying vibrational levels which is observed in reactions of the type Ca* + Cl₂ → CaCl, CaCl* + Cl (see e.g. [15]).

Again, LIF spectra were recorded which now also exhibit three atomic lines' these originate from the 4s4p ³P → 4s5s ³S transitions due to the presence of metastable Ca* in the beam. The lines were used for wavelength calibration; the observed linewidths were in good agreement with those obtained in the opto-galvanic calibration procedure, i.e. Δλ ≈ 0.07 nm.

Lifetime Measurements

With the discharge off fluorescence decay curves for CaCl(A₁,A₂) were measured for different excitation wavelengths. Excitation was accomplished at a distance of 15 cm

from the collimator to guarantee a collision-free environment without quenching of the fluorescence. The fluorescence is recorded time-resolved and is averaged over several hundred laser pulses. A typical time-resolved signal, for an excitation wavelength of 604.61 nm, is shown in both linear and semi-logarithmic representation in Figure 2.

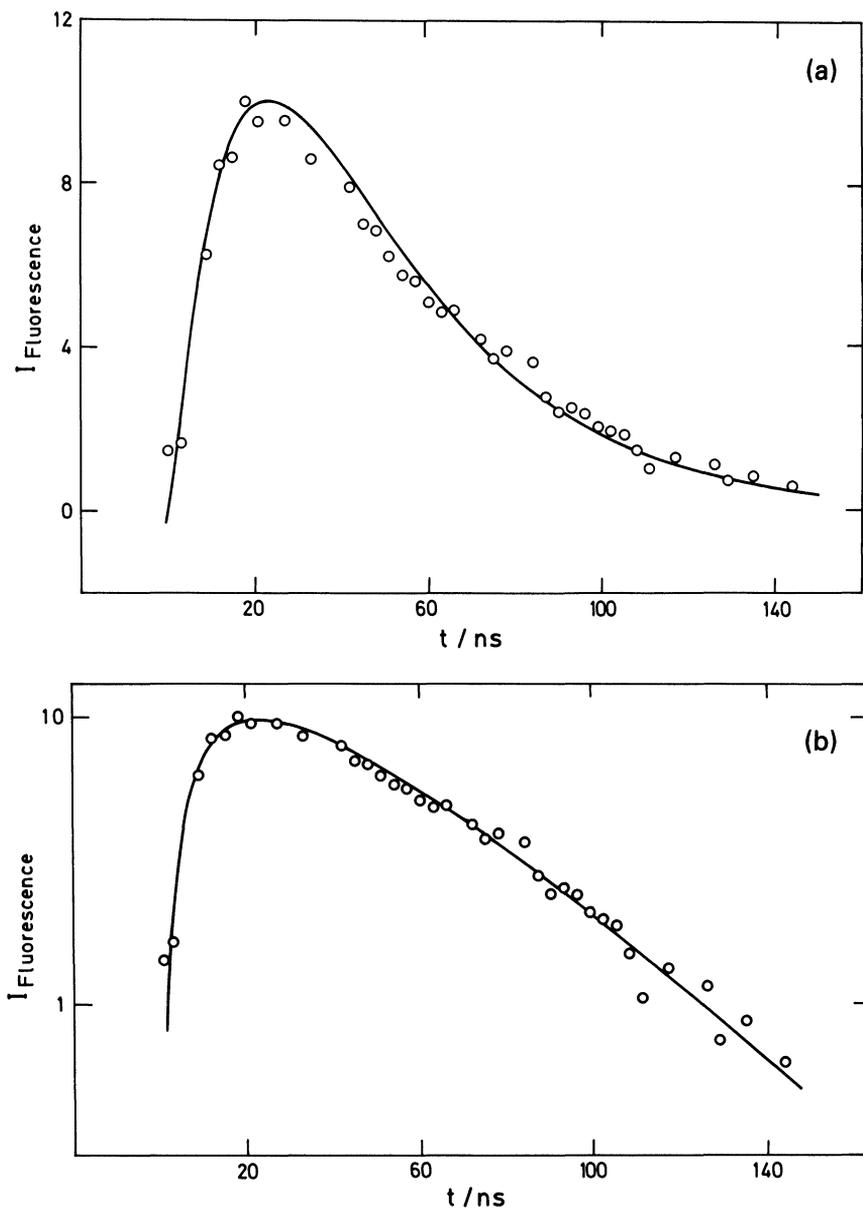


Figure 2 Time-resolved fluorescence from $\text{CaCl}(A_1, \nu' = 1)$ after excitation at $\lambda = 604.62$ nm, (a) linear plot, (b) semi-logarithmic plot.

In order to obtain lifetime values associated with a single vibrational level it would be desirable to excite only one individual (v, J) state. However, pulsed dye laser systems often do not allow this due to their broad linewidth which is usually overlapping a number of rotational transitions in a dense spectrum like that of CaCl. Therefore, we adjusted the linewidth of our laser to embrace a complete bandhead in the spectrum. In this way it is assured that contributions from other than the selected vibrational levels are negligible. This is best fulfilled for the first bandhead in the two Δv -sequences within the tuning range of rhodamine 6G. In the $\Delta v = 0$ sequence this transition corresponds to the $v' = 0 \leftrightarrow v'' = 0$ band and in the $\Delta v = +1$ sequence to the $v' = 1 \leftrightarrow v'' = 0$ band. Thus the lifetimes of $v' = 0$ and $v' = 1$ can be measured.

The time-resolved signals obtained for the various excitation wavelengths in the $X-A_1$ and $X-A_2$ systems were de-convoluted according to the procedure outlined in above, taking into account the RC response of the electronic detection system and the duration of the laser pulse. The values for the lifetimes of CaCl(A_1, A_2) are collected in *Table 2*.

Table 2 Lifetimes (in ns) for CaCl($A^2\Pi$) in the gas phase

State	Quantum number	Lifetime in ns	Pressure in mbar	Ref.
A_1	$v' = 0$	33.0 ± 0.7	$\leq 6 \cdot 10^{-6}$	this work
	$v' = 1$	32.0 ± 0.7	$\leq 6 \cdot 10^{-6}$	this work
A_2	$v' = 0$	33.0 ± 0.7	$\leq 6 \cdot 10^{-6}$	this work
	$v' = 1$	32.0 ± 0.7	$\leq 6 \cdot 10^{-6}$	this work
A_1	$v' \approx 2$	29.4 ± 1.8	$3 \cdot 10^{-5} - 3 \cdot 10^{-3}$	[3]
A_2	$v' \approx 2$	28.4 ± 2.6	$3 \cdot 10^{-5} - 3 \cdot 10^{-3}$	[3]
A_2	$v' = 0$	30.3^a	$\approx 8 \cdot 10^{-4}$	[9]
A_1	$v' = 0$	29.5 ± 1.7	$7 \cdot 10^{-3} - 5 \cdot 10^0$	[5]
A	v'	$28.5 + 0.2 v^b$	—	[7]

^a No error bars given.

^b Theoretical values.

DISCUSSION

There are very few experimental investigations of lifetimes reported for CaCl(A), as has been pointed out in the introduction. The only data available are those of Dagdigian *et al.*,³ and just now those of Berg *et al.*⁵ and Corbett.⁹ The corresponding numerical values are included in *Table 2*.

All three sets of lifetimes are shorter than those measured in this investigation. The possible cause for this difference, although small, could be electronic quenching. For example, the quenching cross section assumed by Dagdigian *et al.* is more than an order of magnitude smaller than the one derived in¹⁶ so that non-radiative desactivation may play a role even at relatively low pressures. In contrast to our experiment all others were conducted at significantly higher pressures, and so back-extrapolation to zero-pressure may result in differences to the "true" radiative lifetime. Hence it is thought that the values for the lifetime of CaCl(A ; $v' = 0, 1$) measured in this investigation are more reliable.

From the two theoretical investigations, in which the electronic transition moment for $\text{CaCl}(A-X)$ was evaluated,^{7,8} lifetimes for $\text{CaCl}(A)$ can be deduced, and these should vary slightly with increasing vibrational quantum number. However, the theoretical values are thought to be too small because of the approximations made for the evaluation of the overlap integrals.

Within the precision of our measurement we cannot resolve a possible change in the lifetime with vibrational quantum number, the more since only $v' = 0$ and $v' = 1$ have been investigated. Experiments to extend our measurements to higher vibrational levels are in progress.

In conclusion, we have shown that it may be important to measure radiative lifetimes under collision-free conditions since it may be difficult to correctly account for quenching processes in the evaluation. Our lifetimes of $\tau \approx 33$ ns are considerably larger, well outside the error bars when comparing them to those reported in the other investigations in which residual quenching could well be present.

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