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Two-photon excitation of the CaI radical

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RESUME

L'excitation des états B et A du radical CaI par un laser visible (620-655 nm) produit une fluorescence dans l'Ultra-Violet entre 315 et 330 nm. Le spectre d'excitation donnant lieu à cette fluorescence se compose d'une dizaine de pics étroits situés à des fréquences coïncidant avec certaines régions des séquences $\Delta v=1$ et 0 (625-642 nm) du spectre d'excitation des systèmes $B^2\Sigma^+-X^2\Sigma^+$ and $A^2\Pi_{1/2}-X^2\Sigma^+$. La plupart des pics peuvent être interpréter comme résultant de l'excitation, fortement amplifiée par résonance, d'un même niveau vibrationnel de l'état $D^2\Sigma^+$ à partir de niveaux successifs de l'état fondamental. L' excitation de l'état D parait due à l'absorption résonante, via les états intermédiaires $B^2\Sigma^+$ and $A^2\Pi_{1/2}$, de deux photons de même fréquence.

ABSTRACT

Fluorescence in the UV (315-330 nm) following visible (620-655 nm) laser excitation of the B and A states of the CaI radical has been detected. The UV excitation spectrum consists of sharp peaks in coincidence with narrow regions of the $\Delta v=1,0$ sequences of the $B^2\Sigma^+-X^2\Sigma^+$ and $A^2\Pi_{1/2}-X^2\Sigma^+$ visible systems. The main peaks are tentatively assigned to resonance-enhanced excitation of a single vibrational level of the $D^2\Sigma^+$ state from successive vibrational levels of the ground state. The excitation process is a one-color two-photon optical-optical-double-resonance via $B^2\Sigma^+$ and $A^2\Pi_{1/2}$ intermediate levels.

INTRODUCTION

Reactions between alkaline earth metals and halogenated compounds have been extensively investigated. Most of these reactions are exothermic and produce vibrationally and electronically excited alkaline earth monohalides. Information on the reaction dynamics can be obtained from the rovibronic population analysis of the alkaline earth monohalide product through either chemiluminescence or Laser Induced Fluorescence. Nevertheless few studies have been concerned with

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reactions of atomic Calcium with Iodides [1,2,3], possibly because of the lack of quantitative spectroscopic data for CaI.

Three band systems, one in the red (626-655 nm), one in the visible (410-440 nm) and a weak one in the violet (312-327 nm) have been assigned to the CaI radical [5-10]. Rotational analysis has been carried out only for the red system, assigned to the $B^2\Sigma^+-X^2\Sigma^+$ and $A^2\Pi-X^2\Sigma^+$ transitions [9].

In this letter we report observation of UV fluorescence following excitation in the 620-655 nm region related to excitation of the $\Delta v=1,0$ sequences of the B-X and $A_{1/2}$ -X system. This fluorescence arises from of a high-lying electronic state excited by a resonance-enhanced two-photon process. Most of the observed features can be assigned to two-photon excitation of a few rovibronic levels of the D state, which is strongly enhanced by resonance through B and $A_{1/2}$ specific levels. A more detailed analysis of the UV excitation spectrum is given elsewhere [11].

EXPERIMENTAL

Calcium moniodine was produced in a Broida-type oven [12] by the reaction of mono-iodine-isopropyl vapor, C_3H_7I , with Calcium vapor produced by heating Ca metal in an alumina crucible and letting it flow with Helium to the reaction zone. Fluorescence was excited by a dye laser pumped with a Nd-Yag pulsed laser (B.M.I.) and detected either through a 0.6 m monochromator with large slits (1 to 5 mm), or using a photomultiplier (RCA IP 28) protected by a cut-off filter. Laser line bandwidth was $\cong 1 \text{ cm}^{-1}$, with an energy of $\approx 1 \text{ mJ}$. Wavelength calibration (with an accuracy of $\approx \pm .20 \text{ cm}^{-1}$) was achieved using a laser induced optogalvanic set-up comprising a Mg-Ne hollow cathode lamp.

RESULTS AND DISCUSSION

The main observations of the present work are summarized in Fig.1, where two excitation spectra recorded while scanning the laser in 620-655 nm spectral region are compared :

i) Fig.1a displays the "red" fluorescence excitation spectrum recorded with the monochromator, set in the same region as the laser excitation, centered at 639 nm. The spectrum exhibits three groups of three broad almost equidistant peaks. From the blue to the red side, the groups are respectively the $\Delta v = +1, 0, -1$ sequences of the $B^2\Sigma^+-X^2\Sigma^+$, $A^2\Pi-X^2\Sigma^+$ systems. In each group the three peaks are, from high to low frequency, respectively the $B^2\Sigma^+-X^2\Sigma^+$, $A^2\Pi_{3/2}-X^2\Sigma^+$

and $A^2\Pi_{1/2}-X^2\Sigma^+$ overlapping sequence bands.

ii) Fig.1b shows the spectrum recorded when the fluorescence is detected using a PM equipped with the cut-off filter (maximum transmission around 320 nm, null between 400 and 650 nm).

Comparison between the spectra of Fig.1a and 1b points out striking features: UV fluorescence is detected very selectively from very narrow regions (within 1-2 cm^{-1}) of the $\Delta v=+1$ and 0 sequence bands of the $B^2\Sigma^+-X^2\Sigma^+$ and $A^2\Pi_{1/2}-X^2\Sigma^+$ systems, and not from any other part of the red excitation spectrum, in particular no "UV fluorescence" is observed from either the $A^2\Pi_{3/2}-X^2\Sigma^+$, $\Delta v=+1,0,-1$ sequence, or the $B^2\Sigma^+, A^2\Pi_{1/2}-X^2\Sigma^+$, $\Delta v=-1$ sequence band excitation. In addition, the peaks occur in regularly spaced groups separated by $\approx 237 \text{ cm}^{-1}$, that is the vibrational interval ($\Delta G_{v+1/2}$) of the $X^2\Sigma^+$ ground state, so that the UV excitation spectrum unexpectedly resembles an emission spectrum.

A plausible interpretation of the UV fluorescence spectrum is a resonance-enhanced-two-photon excitation of an electronic state lying at about twice the B state energy. The obvious candidate is the D state, identified by [10] as responsible for the emission bands observed in the 315-334 nm region. The high selectivity of the process shows that the two-photon excitation requires sharp resonance, and that the observed process is rather a one-color optical-optical double-resonance than a usual two-photon excitation. A similar process involving the D state has been observed in CaCl by Berg, Klynning and Martin [13], who were able to derive molecular constants for the D and X states from the two-photon excitation dispersed fluorescence spectrum.

The two-photon character of the process was checked by the study of the UV fluorescence intensity dependence upon laser intensity measured with a fast photodiode. Its linear variation with the square of the laser intensity supports the hypothesis of a process involving two photons.

Assignment of the OODR spectrum features is not straightforward mainly because of the extreme sequence bands overlap, which according to Reisner *et al.*[9] can result in more than 100 lines/ cm^{-1} . Considering the 1.0 cm^{-1} linewidth of the laser, many rotational transitions involving several vibrational bands can be pumped simultaneously. However, close comparison of the red and UV fluorescence spectra combined with realistic spectroscopic arguments allows to assign most of the "UV spectrum" features. The overall analysis is summarized in Table 1, and the excitation process illustrated in Fig.2.

These preliminary assignments are supported by a more detailed analysis [11], that takes into account the fine structure of 3 involved levels, namely the lower (X), intermediate (A or B) and upper (D) levels. A least squares fit of the wavenumbers of the assigned (D-X) rotational lines allow the determination of the position and rotational constant of the v_D level ($T(v_D) = 31907 \text{ cm}^{-1}$, $B(v_D) = 0.073 \text{ cm}^{-1}$).

CONCLUSION

The spectrum recorded by UV fluorescence detection following laser excitation in the 620-655 nm region has been ascribed to the D-X transition. The excitation process is a one-color two-photon optical-optical double resonance via $B^2\Sigma^+$ and $A^2\Pi_{1/2}$ intermediate levels. Tentative assignments of the spectrum features are presented. Further spectroscopic studies are needed to bear out this analysis and fully characterize the upper state and unambiguously identify the D-X transition. We are presently undertaking the study of the one-photon laser excitation spectrum of the D state collecting the UV fluorescence. An alternate and complementary study is a two-color optical-optical-double-resonance excitation of the D state, via either a A or B level appropriately chosen in the first step, and scanning the second laser in the pertinent region. This investigation is underway at MIT in collaboration with R.W. Field and Z.J. Jakubek.

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Figure 1- CaI excitation spectra recorded by scanning the laser in the 624-654 nm region:

- a) the fluorescence is detected with a monochromator set in the same wavelength region;
- b) the fluorescence is detected using a PM equipped with a cut-off filter with maximum transmission around 320 nm, and null between 400 and 650 nm.

The upper scale refers to the laser excitation frequencies (A-X transition, one-photon excitation). The lower scale refers to the D-X transition absorbing frequencies (two-photon excitation).

Figure 2- Schematic diagram displaying tentative assignments for the UV fluorescence excitation spectrum features.

Table 1

Features of the resonance-enhanced two-photon excitation spectrum of CaI:
Wavelengths, relative intensities, wavenumbers, and tentative assignments

λ_{laser} (nm)	I^a	$h\nu$			$2 h\nu$			$T(D^2\Sigma^+)^c$ (cm ⁻¹)
		ν (cm ⁻¹)	assignment ^b		ν (cm ⁻¹)	assignment		
			ν^o	ν_x		ν	ν_x	
(1) 625.43	5	15984.5	2 _B	1	31969.0	ν_D+1	1	<u>32167</u>
(2) 626.08	20	15968.0	2 _B	1	31936.0			
(3) 626.28	18	15962.9	1 _B	0	31925.8	ν_D	0	<u>31907</u>
(4) 626.64	46	15953.7	1 _B	0	31907.4			
(5) 626.75	58	15950.9	1 _B	0	31901.8			
(6) 631.39	100	15833.7	2 _A	1	31667.4	ν_D	1	31907
			1 _A	0		ν_D-1	0	31644
(7) 631.70	12	15825.9	-	-	31651.8			
(8) 632.12	8	15815.4	1 _A	0	31630.8	ν_D-1	0	31644
(9) 635.71	5	15726.1	2 _B	2	31452.2	ν_D	2	<u>31907</u>
(10) 636.08	26	15716.9	2 _B	2	31433.8			
636.11 ^s		15716.2	2 _B	2	31432.4			
(11) 640.66	8	15604.7	4 _A	4	31209.4	ν_D+1	1	32167
			3 _A	3		ν_D	3	31907
(12) 641.13	11	15593.2	2 _A	2	31186.4	ν_D-1	0	31644

Italic numbers refer to the two-photon spectrum features displayed in Fig. 1

^aIntensity relative to the strongest peak (631.39 nm)

^bA designates the A² $\Pi_{1/2}$ component of the A state

^c*T(D² Σ^+)* is the vibronic origin of the upper level (relative to the X² Σ^+ , *\nu*=0, *J*=1/2 level). Underlined T Values have been obtained by a least squares fit of the corresponding features of the two-photon excitation spectrum.

^sshoulder