AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **82**, 3491 (1985); doi: 10.1063/1.448929
View online: http://dx.doi.org/10.1063/1.448929
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/82/8?ver=pdfcov
Published by the AIP Publishing

Laser induced fluorescence of the MgCa molecule

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(Received 15 October 1984; accepted 17 December 1984)

Using the radiation of several ion laser lines and of a tunable dye laser, the first gas phase spectra of the MgCa molecule have been obtained. The laser induced fluorescence spectra have been assigned to the $A\ ^1\Sigma^+$–$X\ ^1\Sigma^+$, $B\ ^1\Pi$–$X\ ^1\Sigma^+$, and the $C\ ^1\Sigma^+$–$X\ ^1\Sigma^+$ systems. The quantum numbers of the levels belonging to the $X\ ^1\Sigma^+$ ground state were determined using a quantum mechanical, variational method. The vibrational quantum numbers of the excited levels and the assignment to the different electronic states were obtained from a comparison of the measured and calculated Franck–Condon factors which are in very good agreement.

I. INTRODUCTION

It is well known that magnesium and calcium form some of the most prominent absorption features in the spectra of many stellar atmospheres. Knowing the spectra of the Mg_2 and the Ca_2 molecules, a detailed study of the MgCa molecular spectrum is therefore highly desirable for the spectral analysis of a number of cold stellar atmospheres.

In recent years, the homonuclear diatomic alkaline earth molecules Mg_2, Ca_2, and Sr_2 have been the object of several investigations. The Mg_2 A–X system was first analyzed in 1970 by Balfour and Douglas[1] based on absorption measurements. Further information has been provided by Balfour and Whitlock[2] who observed a J dependence of the Franck–Condon factors. Scheingraber and Vidal[3] gave a more detailed evaluation of the discrete and continuous Franck–Condon factors. The molecular constants of the A and X states have then been reevaluated based on an extended data field employing laser induced fluorescence measurements.[4] In addition, Stevens and Krauss carried out *ab initio* calculations of the Mg_2 potential energy curves.[5]

In 1975 Balfour and Whitlock[6] presented absorption spectra of the Ca_2 A–X system. Further investigations of this system were carried out by Sakurai and Broida,[7] Vidal,[8] and Hofmann and Harris[9] using the method of laser induced fluorescence. *Ab initio* calculations on the Ca_2 molecule were carried out by Rosenkrantz *et al.*[10]

The Sr_2 molecule was first observed by Bergeman and Liao[11] who gave some crude molecular constants based on laser induced fluorescence and by computer modeling the modulated continua assuming Morse type potential energy curves. Recently, Gerber *et al.*[12] have analyzed in detail the discrete and continuous spectra from laser induced fluorescence obtaining more accurate Dunham coefficients.

In contrast to the experiments already mentioned, where the molecules were investigated in the gas phase. Miller *et al.* studied diatomic alkaline earth molecules isolated in noble gas matrices.[13] The data obtained from these experiments are incomplete and inaccurate compared with measurements taken in the gas phase. Nevertheless Miller *et al.* observed an absorption band which they assigned to the MgCa molecule.[14,15] This band covers the wavelength region between 530 and 570 nm. The band origin was determined to be 17 274 cm^{-1}. Using an argon matrix the spacing between successive vibronic peaks was interpreted by a vibrational constant of 156 cm^{-1} for the excited state and of 96.6 cm^{-1} for the ground state.[15] Other than that no further data on the MgCa molecule are presently available.

The paper starts with a description of the experimental arrangement. The subsequent section describes the laser induced fluorescence spectra and gives a summary of the molecular transitions observed. Section IV finally provides a detailed analysis of the spectra. It presents the technique for the assignment of the quantum numbers using a quantum mechanical variational method. Furthermore, the molecular constants of the ground and the excited states are presented.

II. EXPERIMENTAL

The MgCa molecules have been generated in a modified concentric heat pipe oven.[16] The vertical tube of the heat pipe oven was filled with sodium and acts as an isothermal heater of well-defined temperature for the horizontal tube of smaller diameter which crosses the vertical tube. Adjusting a pressure of 2.6 bar in the vertical tube a temperature of 980 °C was achieved according to the sodium vapor pressure curve. The horizontal system was filled with a mixture of magnesium and calcium in a helium atmosphere. At a temperature of 980 °C the partial pressure of magnesium is approximately 230 Torr, whereas the partial pressure of calcium is a factor of 40 smaller. For the experiments it is crucial to use a concentric heat pipe oven which allows an independent density and temperature control. A normal heat pipe oven would give rise to severe demixing where eventually calcium is confined by magnesium.

In the concentric heat pipe oven we have Mg_2, Ca_2, and MgCa molecules inside the horizontal tube. The absorption bands of the Mg_2 molecule are known to cover the violet and the UV region of the spectrum,[1,4] whereas the bands of the MgCa molecule are expected to overlap

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with the bands of the Ca_2 molecule in the visible part of the spectrum. Such a superposition of the spectra due to different species may give rise to difficulties in the assignment of the measured lines. However, inside the horizontal tube of the heat pipe oven MgCa molecules are expected to occur with a higher abundance than the Ca_2 molecules because of the partial pressures. As a result, the intensity of the Ca_2 lines should be significantly smaller than the intensity of the lines due to the MgCa molecule. This fact greatly facilitates the assignment.

The experimental arrangement is very simple and straightforward. The horizontal tube of the heat pipe system serves as a fluorescence cell. The radiation of an argon ion and of a krypton ion laser and of a tunable, stabilized, single mode dye laser were used to excite the molecules inside the cell in the gas phase. The resulting laser induced fluorescence was observed by means of a 2 m grating spectrometer. The instrument had a theoretical resolving power of 80 000 in first order.

For an accurate measurement of the line positions spectra were taken on photographic plates (Kodak 103F) and were evaluated on a high precision microphotometer. The fluorescence spectrum was calibrated by means of a thorium reference spectrum[17] generated in a hollow cathode discharge. Both spectra were taken simultaneously to avoid any offset of the two spectra due to thermal or any other long term drifts of the spectrometer.

The relative intensity distribution of the fluorescence lines which is required for a measurement of the Franck–Condon factors, was obtained from photoelectric scans. For this purpose the incident laser beam was modulated and the detector signal was extracted by means of a phase sensitive amplifier.

III. OBSERVED SPECTRA

Since absorption spectra generally provide a very useful survey of the overall spectrum of a molecule, we first tried to observe the MgCa molecule in absorption. However, the exposed plates only showed strong continua and some atomic absorption lines. Apparently, the column density inside the horizontal tube of the heat pipe system was insufficient for obtaining any significant discrete molecular absorption features. We then succeeded to generate laser induced fluorescence spectra which are known to have a significantly higher sensitivity compared to conventional absorption spectra. Several lines of an argon ion and of a krypton ion laser in the range from 454.5 to 568.2 nm were used to pump several transitions from the ground state of the MgCa molecule. From the laser pumped levels of the excited electronic states the molecules radiate back to the ground state and show the typical v'' progressions of laser induced fluorescence as they are associated with bound–bound–bound transitions. Figure 1 shows a typical example taken with the 468 nm line of a krypton ion laser.

All the laser induced transitions of the MgCa molecule which were pumped with the different ion laser lines, are summarized in Table I. A listing of the laser lines is given together with the initial and final rotational and vibrational quantum numbers, the upper electronic state, and the term value of the excited level as determined from the analysis given below.

As known already from other diatomic alkaline earth molecules[3,8,11,12] and from the iodine molecule,[18,19] we also observed structured continua. At an excitation wavelength between 503 and 485 nm these continua die out, indicating a decreasing quantum efficiency of the excited state which might be due to some predissociation. The continua are due to bound–bound–free transitions in which the molecules relax from the laser excited level back to the dissociation continuum of the ground state.

Around 521 nm the (0, 0) band of the MgH A–X system was found to be the most prominent molecular impurity. At elevated temperatures we also obtained several very weak laser induced v'' progressions of the Ca_2 molecule which could be easily distinguished based on the results of Ref. 8.

From an inspection of Table I it is also apparent that the coverage of the laser excited levels is rather incomplete around the minimum of the A state. For this reason we took further laser induced fluorescence spectra using a tunable, stabilized, single mode dye laser. These spectra were visually optimized by watching the laser

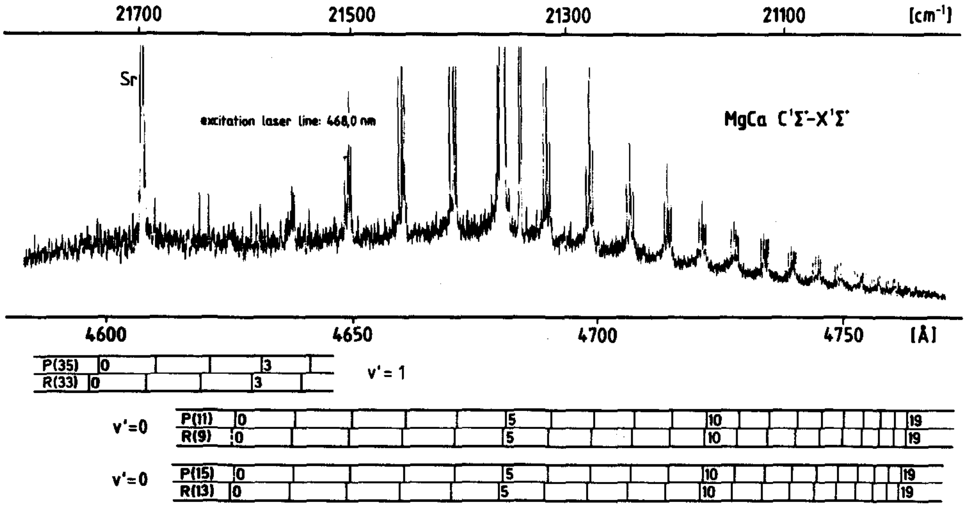

FIG. 1. Laser induced fluorescence spectra excited by the 468 nm line of a krypton ion laser.

TABLE I. Ion laser induced transitions.

Laser line (Å)	v'	J'	Excited state	v''	J''	Term value (cm^{-1})
4545 (Ar)	4	72	*C*	3	71	22 494.24
4579 (Ar)	2	56	*C*	1	57	22 131.90
4658 (Ar)	5	59	*B*	0	58	21 720.78
4680 (Kr)	0	10	*C*	5	9	21 650.22
	0	14	*C*	5	15	21 659.00
	1	34	*C*	9	33	21 855.80
4727 (Ar)	3	62	*B*	1	63	21 496.58
	0	41	*C*	14	40	21 791.18
	0	36	*C*	13	35	21 757.17
4762 (Kr)	32	62	*A*	4	63	21 467.73[c] *X*
	32	54	*A*	4	53	21 400.92[c] *X*
	3	55	*B*	4	56	21 419.92
	2	80	*B*	4	80	21 602.47
4825 (Kr)	29	82	*A*	6	81	21 397.52[c] *X*
	29	43	*A*	3	44	21 032.21[c] *X*
	31	37	*A*	8	36	21 193.08[c] *X*
5145 (Ar)	15	96	*A*	0	95	20 044.95
5208 (Kr)	16	48	*A*	4	47	19 568.53
	15	49	*A*	1	50	19 447.42
	16	52	*A*	4	53	19 603.78
5309 (Kr)	13	23	*A*	2	24	19 010.90
	11	80	*A*	0	79	19 275.42
	12	78	*A*	3	77	19 381.10
5682 (Kr)	3	74	*A*	1	75	18 044.87
	4	82	*A*	6	83[b]	18 267.44[c] *X*
	5	32	*A*	4	33[a]	17 897.57

[a] ^{25}Mg^{40}Ca.

[b] ^{26}Mg^{40}Ca.

[c] Term values marked by an *X* have not been used for the Dunham-type coefficients of the excited states.

induced fluorescence directly on the spectrometer while tuning the dye laser. Figure 2 shows a typical example. All the laser induced fluorescence series which have been obtained by means of the tunable dye laser are summarized in Table II together with the upper and lower state quantum numbers of the pump transition and the term value of the excited state.

IV. RESULTS

As mentioned above we did not succeed to generate absorption spectra of the MgCa molecule which would allow a direct assignment of the quantum numbers simply on the basis of the band structure of these spectra, and in particular, of the isotope shift. In addition, we did not

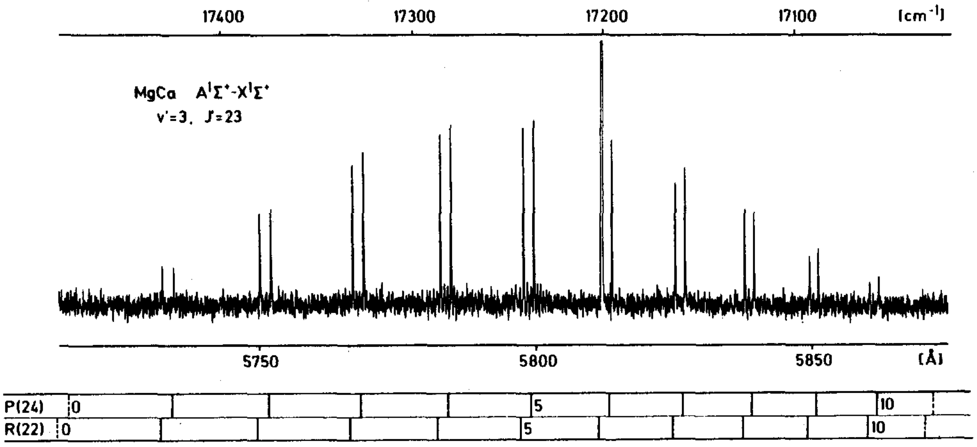

FIG. 2. Laser induced fluorescence spectrum excited by a stabilized single mode dye laser at 581.18 nm.

TABLE II. Dye laser induced transitions of the A–X system.

Laser line (Å)	v'	J'	v''	J''	Term value (cm^{-1})
5737.95	4	34	5	33	17 772.95
	4	37	5	38	17 794.00
5766.37	3	67	7	68	17 948.79
	5	32	12	31	17 910.53
5775.86	3	48	5	49	17 734.32
5811.75	3	23	6	22	17 557.90
5814.15	3	22	6	23	17 553.37
	3	46	8	47	17 715.75
5819.20	3	8	6	7	17 510.60
5823.91	3	50	10	49	17 753.65
5843.51	2	34	5	35	17 466.30
	3	31	9	32	17 601.14
5843.53	2	65	10	64	17 771.28
5850.87	2	62	10	61	17 733.64
5877.35	2	36	8	35	17 480.33
5877.49	2	26	7	27	17 418.03
5879.96	2	36	8	37	17 480.33
5882.54	2	16	7	15	17 375.42
5902.29	2	45	12	44	17 553.14
5919.69	2	43	14	42	17 535.59

observe any collision induced satellite lines in the fluorescence spectra which would greatly facilitate the identification of the J quantum numbers. For this reason the assignment of the quantum numbers was not at all trivial and we had to resort to more sophisticated methods which are described in the following.

A. The $X\,^1\Sigma^+$ ground state

The analysis of the spectra was started with a tentative assignment of the quantum numbers belonging to the individual measured lines. This assignment was based on preliminary and approximate molecular constants for the $X\,^1\Sigma^+$ ground state of the MgCa molecule which resulted from an interpolation plotting the lowest order molecular constants and the dissociation energy of the Ca_2 and the Mg_2 molecule vs the reduced mass. Already at this stage of the investigations it was evident from the extent of the observed v'' progressions that the observed spectra had to be due to transitions to the $X\,^1\Sigma^+$ ground state of the MgCa molecule.

The molecular constants are generally obtained from a minimum variance, linear, unbiased fit of the measured line positions.[20] The observed line frequency $\bar{\nu}$ is given by

$$\bar{\nu} = T'(v', J') - T''(v'', J''), \qquad (1)$$

where $T'(v', J')$ and $T''(v'', J'')$ are the term values of the upper and lower electronic state, respectively. The term value $T(v, J)$ can be given by a Dunham-type expansion using mass reduced variables

$$T(v, J) = \sum_{ik} A_{ik}(v + 1/2)^i[J(J+1) - \Lambda^2]^k \mu_r^{-(i/2)-k}, \qquad (2)$$

where the A_{ik} are the Dunham type coefficients and μ_r is the reduced mass normalized with respect to the reduced mass of the most abundant isotope combination ^{24}Mg ^{40}Ca. The electronic angular momentum Λ is equal to 0 for Σ states and equal to 1 for Π states.

In our initial least squares fit a separate constant was assigned to every laser pumped level $T'(v', J')$, whereas the term values $T''(v'', J'')$ of the ground state were given by the Dunham-type expansion in Eq. (2). In this manner an analysis of the molecular ground state can be carried out without any knowledge of the particular excited electronic state and without knowing the vibrational quantum numbers v' of the laser pumped levels.

The v'' quantum numbers of the laser induced progressions were determined by following the individual progressions down to $v'' = 0$ assuming favorable Franck–Condon factors as verified below. The J'' quantum numbers of the ground state levels were established in the following manner:

(1) From the interpolated value of B''_v and the separation between the P and R lines a tentative J'' value was obtained. Because of the uncertainty with respect to the exact value of B''_v we initially had to allow for a possible J'' numbering which could have been off by ±1.

(2) We started the least squares fit using the three v'' progressions which showed the smallest splitting of the P and R lines. In this manner the J'' quantum numbers were kept sufficiently small so that contributions due to the centrifugal distortion constants were expected to provide only a minor correction to the exact term values of the ground state. In contrast to the situation for the calcium isotopes the relative abundance of the different magnesium isotopes requires also a consideration of the less abundant isotopes ^{25}Mg and ^{26}Mg. The Dunham-type expansion was therefore applied using mass reduced variables as indicated in Eq. (2). Hence $3^3 = 27$ least squares fits for three different isotope combinations and three different values of J'' were carried out. Out of these, only four gave an acceptable standard error smaller than 0.1 cm^{-1}.

(3) Using a technique recently proposed by one of us[21] which is based on an inverted perturbation approach (IPA),[22,23] the four remaining least squares fits were tested with respect to their quantum mechanical significance. The method investigates to what extent the measured term values can be described as quantum mechanical energy eigenvalues of a rotating vibrator. Only for one of the four remaining least squares fits a satisfactory result within the standard error of the measurements was obtained. The isotope combinations of that particular fit turned out to be ^{24}Mg ^{40}Ca for all three initial v'' progressions.

(4) Finally, all the remaining v'' progressions were gradually added to the least squares fit of the initial three v'' progressions. In order to keep the standard error within its own standard error,[20] more Dunham-type coefficients had to be added as the data field of the molecular ground

state was extended. The final set of molecular constants was tested again by the IPA technique. With the correct J'' numbering the IPA technique in addition confirmed the preliminary v'' numbering.[21]

In this manner the quantum numbers J', J'', and v'' for all measured line positions were unambiguously determined. The data field of the ground state covered by all the laser induced fluorescence measurements is shown in Fig. 3. The Dunham-type coefficients and their standard errors as obtained in the final least squares fit, are summarized in Table III. The total number of measured line positions was 1699 and the total standard error amounted to 0.054 cm^{-1}.

Furthermore, an IPA potential energy curve of the molecular ground state was calculated resulting in a standard error of 0.033 cm^{-1}. The G_v and the B_v values and the classical turning points are given in Table IV.

The dissociation energy of the X state was determined to be $D_e = 691.5 \pm 0.5\ \mathrm{cm}^{-1}$. In addition, we evaluated a C_6 constant which describes the long range part of the potential energy curve over a range $8.0 < R < 9.5$ Å according to $U(R) = D_e - C_6/R$ with $C_6 = 9.5 \times 10^6\ \mathrm{cm}^{-1}\ \text{Å}^6$. This value is reasonably close to the theoretical value $C_6 = 5.515 \times 10^6\ \mathrm{cm}^{-1}\ \text{Å}^6$ which was obtained from a relation given by Dalgarno.[24]

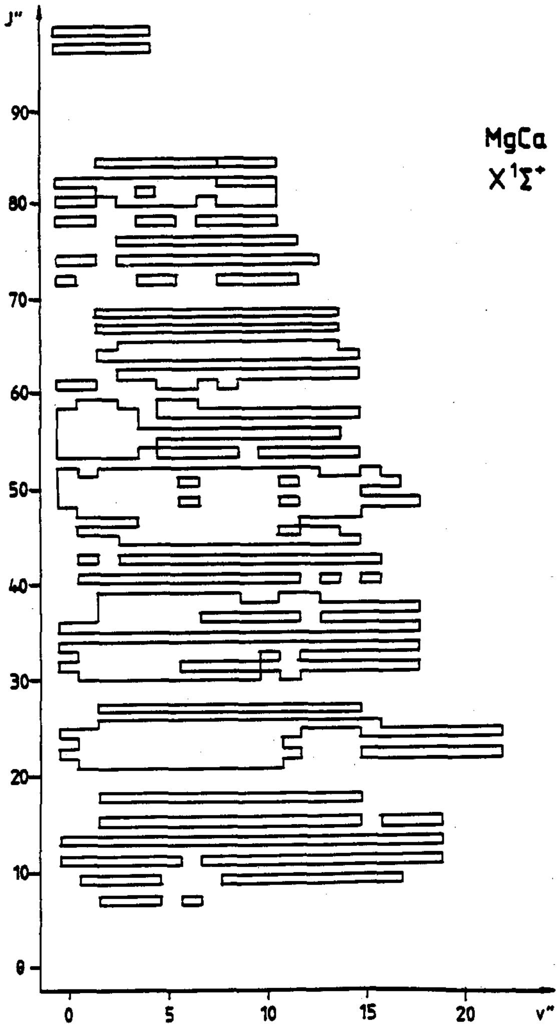

FIG. 3. Data field of the MgCa ground state.

TABLE III. Dunham-type coefficients and their standard errors for the $X\,^1\Sigma^+$ ground state. All values are given in cm^{-1}.[a]

A''	0	1	2	3
0		6.8962-2 (21)	−3.613-7	−5.23-12 (26)
1	60.257 (22)	−1.934-3 (20)	0.18-8 (45)	−2.00-12 (31)
2	−1.6525 (62)	3.09-5 (56)	−0.72-8 (11)	3.11-13 (65)
3	2.584-2 (72)	−6.40-6 (65)	1.105-9 (97)	−5.00-14 (37)
4	−7.84-4 (36)	4.30-7 (32)	−4.74-11 (25)	
5	1.159-5 (66)	−1.063-8 (58)		

[a] $N = 1699$, $\sigma_{\mathrm{tot}} = 0.054\ \mathrm{cm}^{-1}$.

B. The excited states

The preceding analysis gave an unambiguous determination of the molecular constants of the $X\,^1\Sigma^+$ ground state and gave the term values for all the laser excited upper levels. We were therefore left to assign the excited electronic states and to determine the vibrational quantum numbers v' of the laser excited levels. The J' quantum numbers are, of course, already known from the analysis of the molecular ground state because of the selection rules. Nearly all v'' progressions showed simple doublets of P and R lines, most of which we assumed to originate from $^1\Sigma^+$–$^1\Sigma^+$ transitions. However, there was also a Q series which can only be explained by a $^1\Pi$–$^1\Sigma^+$ transition.

In order to obtain an unambiguous assignment of the upper excited electronic states we started with a tentative assignment of the v' quantum numbers based

TABLE IV. The IPA potential energy curve of the MgCa $X\,^1\Sigma^+$ state.

v	G_v	$R_{\min}$(Å)	$R_{\max}$(Å)	B_v
0	29.73	3.867 337	4.258 140	0.067 991 9
1	86.76	3.763 416	4.456 460	0.066 135 1
2	140.68	3.701 321	4.617 155	0.064 270 5
3	191.64	3.656 251	4.765 571	0.062 392 1
4	239.74	3.621 014	4.909 228	0.060 500 4
5	285.06	3.592 182	5.051 758	0.058 597 6
6	327.67	3.567 730	5.195 400	0.056 685 1
7	367.63	3.546 352	5.341 804	0.054 761 1
8	405.01	3.527 269	5.492 391	0.052 821 8
9	439.87	3.510 237	5.648 547	0.050 860 4
10	472.26	3.495 445	5.811 769	0.048 868 8
11	502.21	3.483 030	5.983 782	0.046 837 4
12	529.77	3.472 731	6.166 669	0.044 755 3
13	554.96	3.464 083	6.363 008	0.042 611 0
14	577.81	3.456 678	6.576 052	0.040 392 5
15	598.32	3.450 237	6.809 962	0.038 087 8
16	616.52	3.444 622	7.070 141	0.035 685 2
17	632.43	3.439 853	7.363 797	0.033 173 7
18	646.10	3.435 770	7.701 104	0.030 548 6
19	657.60	3.432 297	8.091 650	0.027 839 2
20	667.08	3.429 389	8.550 300	0.025 077 5
21	674.71	3.427 008	9.100 624	0.022 356 9

on the intensity distribution of the v'' progressions and on the spacing of the laser excited term values. On the basis of this tentative assignment we calculated preliminary molecular constants for every individual excited state in a least squares fit. With these constants we calculated the RKR potential energy curve of the excited electronic state. Using the potential energy curve of the ground state obtained above, the Franck–Condon factors were calculated for the observed transitions. A comparison with the photoelectrically measured line intensities immediately verified whether or not the initial tentative assignment was correct. As already known from previous investigations of the alkaline earth molecules[2,3,8,12] there is a strong J dependence of the Franck–Condon factors. This J dependence was also observed in case of the MgCa molecule and was accounted for in all calculations of the Franck–Condon factors.

1. $C\ ^1\Sigma^+$ state

The assignment of the excited electronic states was started with four v'' progressions showing an intensity distribution with one broad maximum. Such a distribution is the hallmark for a v'' progression originating from states with $v' = 0$. The energy separation of these four term values with $v' = 0$ also gave a reasonable B'_0 value which

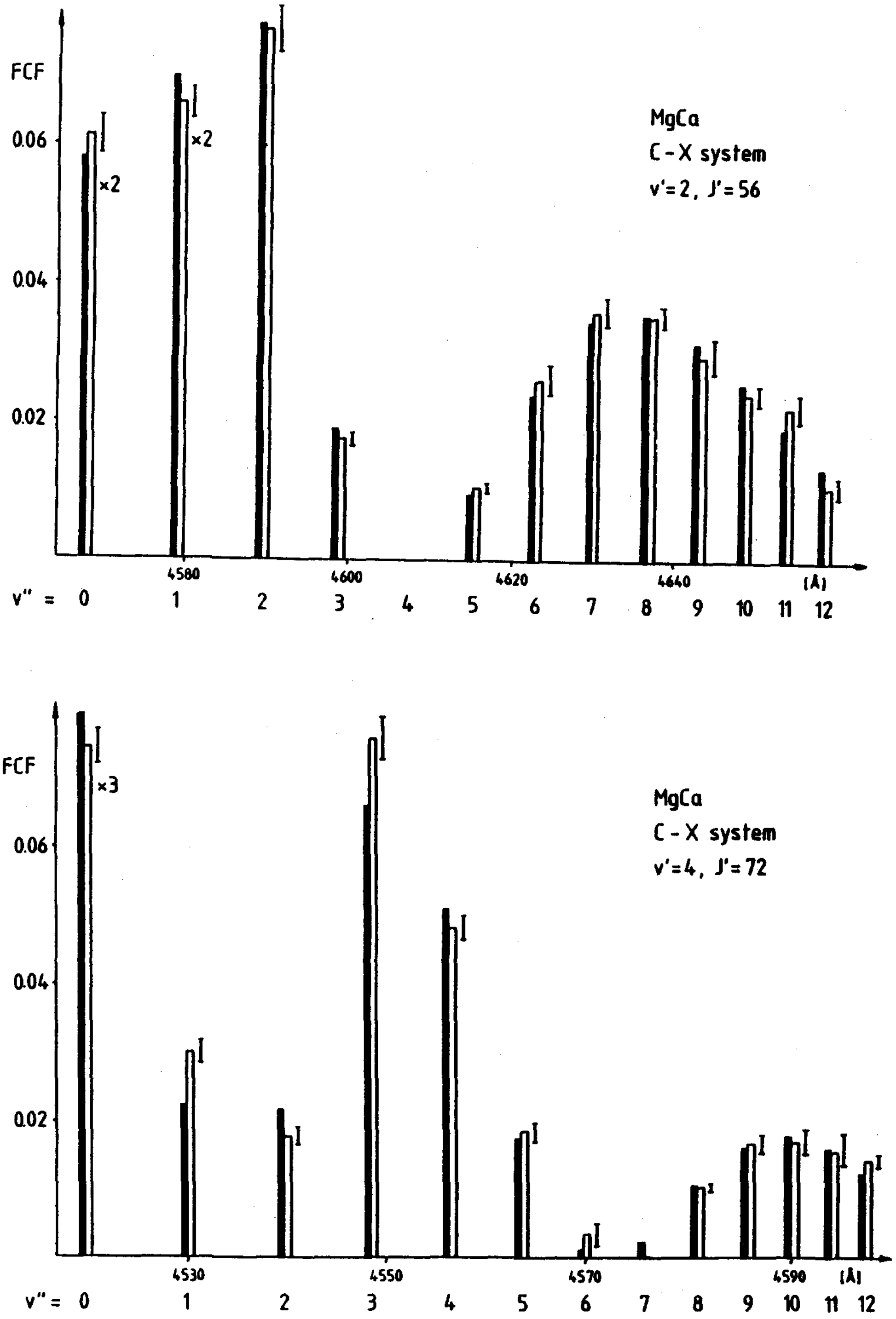

FIG. 4. Comparison of the measured (open bars) and calculated (solid bars) Franck–Condon factors for two v'' progressions of the C–X system.

was used to approximately extrapolate the term values of the rotationless molecule from the measured term values with $J > 0$. In this manner three additional levels with $v' = 1, 2$, and 4 could be identified. Based on these measured term values Dunham-type coefficients were determined in a least squares fit. The molecular constants were used for calculating the RKR potential and the Franck–Condon factors. As shown in Fig. 4 an excellent agreement was obtained between the measured and the calculated Franck–Condon factors. This verifies the vibrational quantum numbers v'.

2. $A\,^1\Sigma^+$ state

Our investigations revealed term values of excited levels in a spectral region where Miller *et al.*[14,15] already observed an absorption feature from matrix isolated magnesium and calcium. In this case the vibrational assignment was more cumbersome. Since there was no typical intensity distribution indicating an excited state with $v' = 0$ or $v' = 1$ we could determine initially only a relative vibrational numbering whose absolute value was off by some integer value from the true vibrational numbering. This problem was eventually resolved by calculating the Dunham-type coefficients, the RKR potential, and the corresponding Franck–Condon factors for every possible vibrational numbering. In this manner we finally found an unambiguous assignment of the vibrational quantum numbers v' for all measured term values belonging to this electronic system. Two examples in Fig. 5 taken at large values of v' show again the good agreement between the measured and calculated Franck–Condon factors. It should be pointed out that the required RKR potential was obtained from a preliminary set of Dunham-type coeffi-

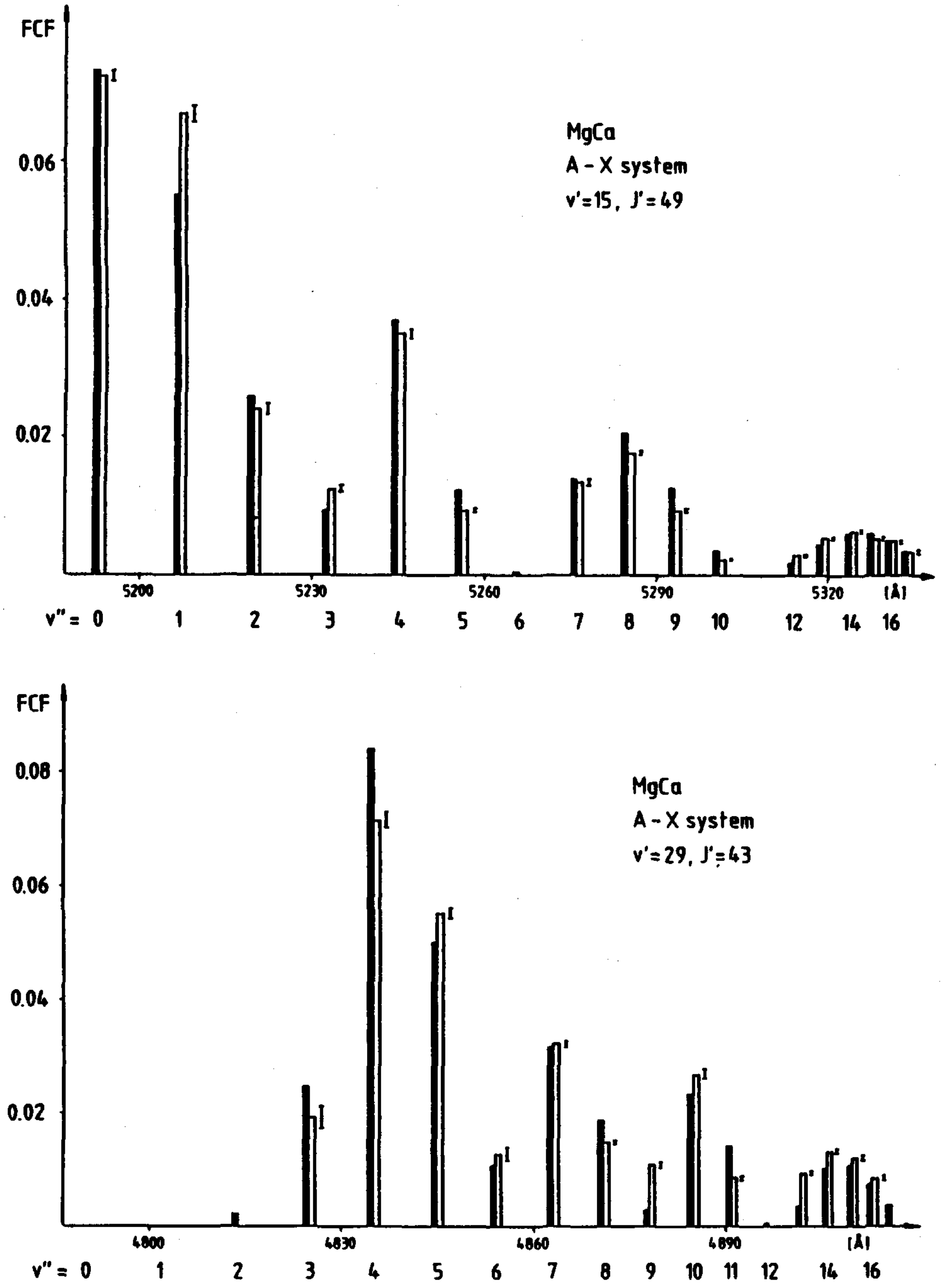

FIG. 5. Comparison of the measured (open bars) and calculated (solid bars) Franck–Condon factors for two v'' progressions of the A–X system. As explained in the text, the calculated Franck–Condon factors originate from an RKR potential, which is based on a preliminary set of Dunham-type coefficients, which differ from the ones given in Table V and which have been determined in a least squares fit including the perturbed levels with $28 < v' < 33$.

cients which has been obtained in a least squares fit including all levels up to $v' = 32$. The standard error of this fit was rather large. In the final least squares fit the levels with $28 < v' < 33$ had to be eliminated because they are perturbed as discussed below. In this manner the standard error of the final least squares fit was significantly reduced. For this reason the final set of Dunham-type coefficients, as given in Table V, is, of course, not able to define the potential energy curve all the way up to $v' = 32$. However, for determining the quantum number v' a potential energy curve of limited accuracy appears to be adequate as shown in Fig. 5.

From all the measured term values which were excited by one of the ion laser lines, we were able to assign 15 different levels to one common electronic state. The values of v' cover a range from $v' = 3$ to $v' = 32$. As indicated in Table I we also found two v'' progressions which originate from the less abundant isotope combinations ^{25}Mg ^{40}Ca and ^{26}Mg ^{40}Ca. As already indicated, we then generated further laser induced fluorescence spectra using a tunable, stabilized, single mode dye laser in order to obtain a better definition of the electronic state around its potential minimum. According to Table II, 20 additional term values of the excited state were obtained. Since all the 35 measured term values gave rise to doublets of P and R lines the excited electronic state had to be the $A\ ^1\Sigma^+$ state. This was further supported by the existence of a $^1\Pi$ state to be presented below.

TABLE V. Dunham-type coefficients and their standard errors for the $A\ ^1\Sigma^+$, $B\ ^1\Pi$, and $C\ ^1\Sigma^+$ states. All values are given in cm^{-1}.[a]

A state constants

A'	0	1	2	3	4
0	16 949.98 (11)	0.102 053 (35)	−1.602-7	3.71-11 (31)	−3.31-15 (22)
1	162.906 (80)	−1.566-3 (23)	−5.74-8 (51)		
2	−1.562 (21)	2.466-4 (90)	3.72-9 (29)		
3	6.44-2 (18)	−2.253-5 (87)			
4	−1.869-3 (49)	6.08-7 (24)			

B state constants

A'	0	1	2	
0	20 666.84 (93)	9.4077-2 (40)	−1.818-7	
1	135.33 (39)			$q = -3.86\text{-}5$
2	−0.696 (44)			

C state constants

A'	0	1	2
0	21 582.552 (28)	8.8279-2 (29)	−1.999-7
1	117.325 (15)	−9.46-4 (23)	
2	−2.587 (24)		

[a] $N = 1699$, $\sigma_{\text{tot}} = 0.054$ cm^{-1}.

3. *B* $^1\Pi$ *state*

After the vibrational assignment of all levels belonging to the A and the C state we were finally left with four v'' progressions among which we identified one Q series. All four levels could be identified by a relative vibrational numbering whose absolute value was determined by the corresponding Franck–Condon factors similar to the procedure applied in case of the A state. The Q series also identified these levels as belonging to the $B\ ^1\Pi$ state. Figure 6 shows again a very good agreement between the measured and the calculated Franck–Condon factors.

In order to include a Q series in the least squares fit one has to account for the Λ-type doubling of the $B\ ^1\Pi$ state. In view of the insufficient number of term values for defining the potential energy curve we calculated the lowest order Λ-doubling constant q according to the relation given by Van Vleck[25]:

$$q = 2B_v^2 l(l+1)/\bar{\nu}(\Pi\Sigma), \tag{3}$$

where $\bar{\nu}(\Pi\Sigma)$ is the energy separation between the $B\ ^1\Pi$ state and the perturbing state. Since the q constant contributes only a minor correction to the term values, the molecular constants required by Eq. (3) were taken from an initial least squares fit and were improved in subsequent iterations. For the case where the $A\ ^1\Sigma^+$ state is the perturbing state, $q = 9.53 \times 10^{-6}$ cm^{-1} and for the $C\ ^1\Sigma^+$ state being the perturbing state we have $q = -3.86 \times 10^{-5}$ cm^{-1}. In order to decide which one of the two states is the perturbing one, a knowledge of the molecular dissociation is required.[26] This cannot be determined unambiguously from the available measurements which do not define the potential energy curves sufficiently close to the dissociation limits (see the discussion given below).

C. The Dunham-type coefficients of the excited states

In case of the X state the determination of the Dunham-type coefficients was already explained in detail. As can be seen from the data field given in Fig. 3 the ground state molecular constants are very well defined by a highly redundant set of measurements. For the excited states, however, the situation is quite different. As shown in Tables I and II we have in some cases a rather sparse data field with a small number of laser excited levels which is insufficient to generate a reliable set of Dunham-type coefficients and to accurately define the potential energy curves of the different excited electronic states. For the B and the C state it turns out that we had to use almost as many Dunham-type coefficients as there are laser excited levels in order to obtain a sufficiently small standard error in the least squares fit. This implies that

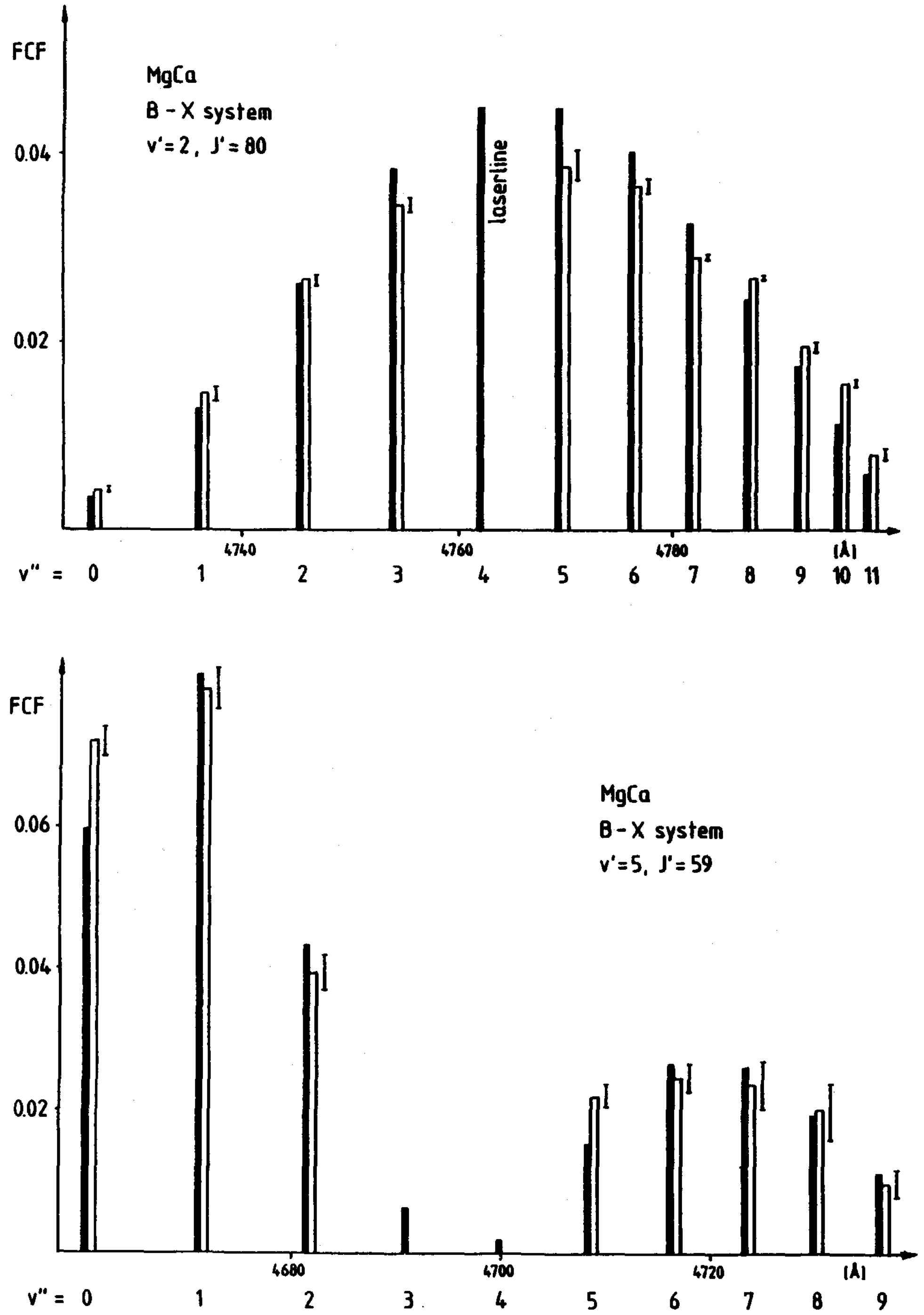

FIG. 6. Comparison of the measured (open bars) and calculated (solid bars) Franck–Condon factors for two v'' progressions of the B–X system.

the specific set of coefficients is to some degree arbitrary because in such a situation several sets of constants can reproduce the measured term values equally well. However, for calculating the potential energy curves the different sets of Dunham-type coefficients may lead to widely different results. For this reason we selected a set of coefficients which not only described the measured term values but which obeys also the well-known Kratzer relation[27] $D_e = 4B_e^3/\omega_e^2$. This relation is generally valid as long as the term values to be described can be given by a perturbation approach.[28-32] The final set of Dunham coefficients was obtained after three iterations in which the A_{02} constants were fixed for all electronic states. The results for the X, A, B, and C states are summarized in Tables III and V. This final set of coefficients was obtained in a simultaneous least squares fit of all three different electronic systems observed. The measured line positions used in the final least squares fit are available as a PAPS document.[33]

In performing the global least squares fit we have assigned individual term values to six levels which are marked by an X in Table I. The reason for this was that the levels with $v' > 28$ show strong indications of perturbations. Furthermore, an unphysically large number of constants is required to bridge the gap in the data field with $16 < v' < 29$ where no laser induced fluorescence could be detected. Similarly, the level with $v' = 4$ and $J' = 82$ requires more than one additional Dunham

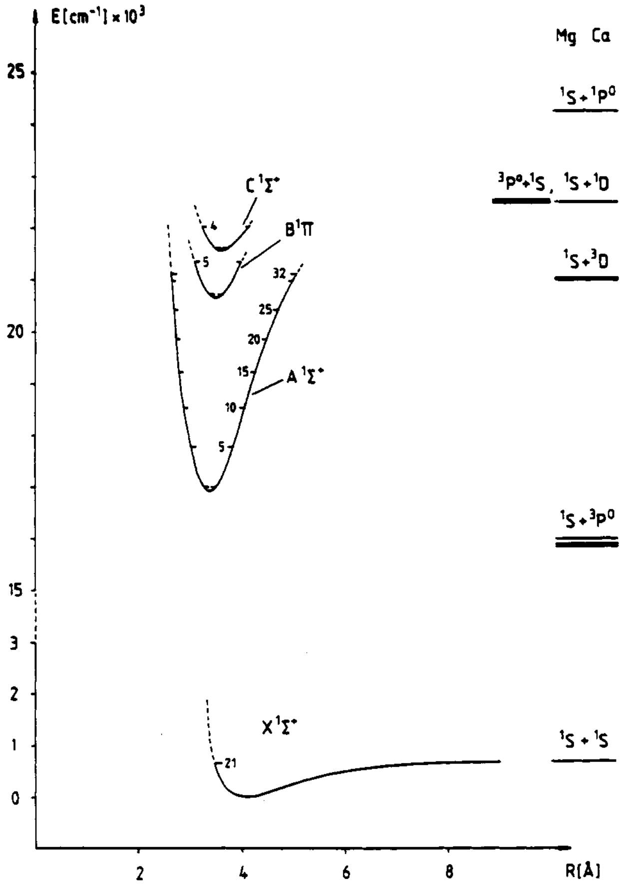

FIG. 7. Potential energy curves of the *X*, *A*, *B*, and *C* states of the MgCa molecule.

coefficient and was therefore described by a separate term value listed in Table I.

V. DISCUSSION

Our final results of the potential energy curves are shown in the plot of Fig. 7. The solid lines represent the parts of the potential energy curves which are defined by measurements. On the right side of Fig. 7 the energy levels of the separated atoms are given. The measurements have revealed two $^1\Sigma^+$ states and a $^1\Pi$ state as excited states. States of this kind could dissociate either into the Mg ^1S + Ca ^1D limit or into the Mg ^1S + Ca $^1P^0$ limit. The next limit which is capable of forming singlet states, occurs around 34 000 cm^{-1} (Mg $^1P^0$ + Ca ^1S). It is rather high and somewhat unlikely as a possible dissociation limit for the observed excited states. We therefore suspect that the $A\ ^1\Sigma^+$ state dissociates into the Mg ^1S + Ca ^1D limit, whereas the $B\ ^1\Pi$ and $C\ ^1\Sigma^+$ states dissociate into the Mg ^1S + Ca $^1P^0$ limit. In this case the $C\ ^1\Sigma^+$ state would also be the relevant perturbing state for the Λ-type doubling constant q of the $B\ ^1\Pi$ state as assumed in our final least squares fit.

It should, however, be pointed out that the existing measurements do not yet allow a unique assignment of the appropriate dissociation limits. The situation is somewhat ambiguous and has to await either further measurements or an *ab initio* calculation which would be more involved than the previous Mg_2 and the Ca_2 calculations[5,10] because of the missing gerade–ungerade symmetry.

A further interesting aspect of our measurements is indicated in Fig. 8 where the *A* state is shown with all measured term values which were obtained with one of the ion laser lines. The term values reached by the tunable dye laser are not explicitly shown since they are all crowded close to the minimum of the potential energy curve. The vertical bars in Fig. 8 indicate the energy range which could be covered by some particular ion laser line or by the tunable dye laser assuming an excitation from one of the thermally populated bound levels of the electronic ground state. Open bars correspond to those ion laser lines for which no laser induced fluorescence has been observed at all, whereas hatched bars mark those lines which give rise to laser induced fluorescence. In trying to generate laser induced fluorescence spectra one

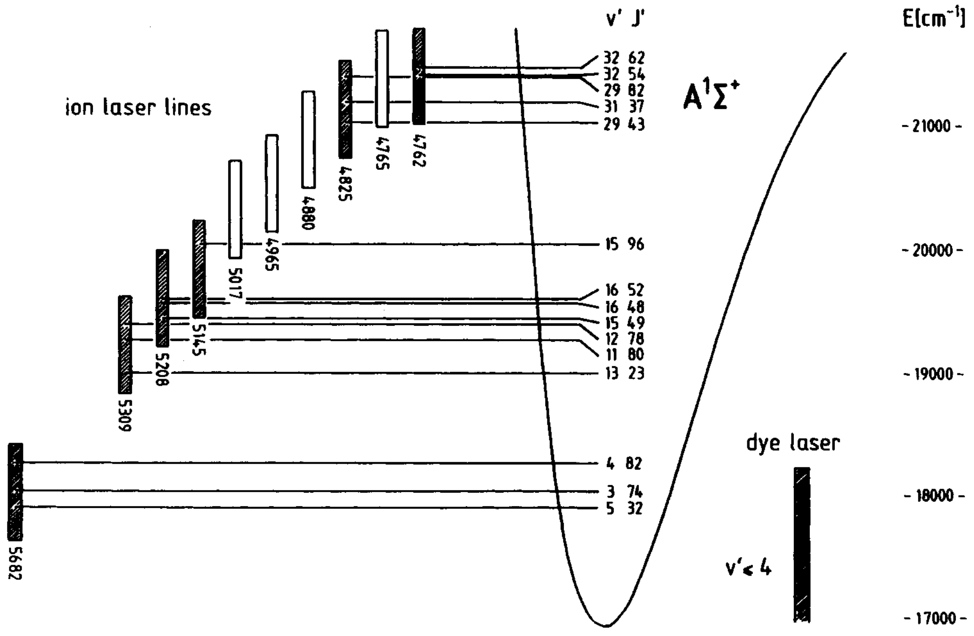

FIG. 8. Potential energy curve of the *A* state of the MgCa molecule showing all the term values which have been excited by one of the laser lines. The vertical bars indicate the energy range which could be covered by a particular ion laser line, or by the tunable dye laser assuming an excitation from one of the thermally populated bound levels of the ground state. The open bars mark those ion laser lines which do not give rise to any laser induced fluorescence at all. It is suspected that the extremely small quantum efficiency of the excited levels with 15 < v' < 28 originates from predissociation due to a perturbing triplet state.

notices already from Table I that we did not succeed to obtain spectra for the ion laser lines between 515 and 485 nm although some of the most intense laser lines are located in this spectral region. In this context we also recall that the laser induced continuous spectra started to die out as the laser was tuned beyond 503 nm towards shorter wavelengths indicating a decreasing quantum efficiency of the excited state possibly due to some predissociation. Furthermore, we observed perturbations in fitting the measured term values with $v' > 28$. For some of the rather weak laser lines at shorter wavelengths we obtained again fairly strong fluorescence. All of this evidence leads one to believe that for the spectral region indicated some sort of interaction with another electronic state might be responsible for the disappearance of the laser induced fluorescence and for the perturbations of the levels at elevated values of v'. We suspect that a triplet state which has not yet been observed directly, might be responsible for this.

Finally, it should be noted that our gas phase molecular constants differ dramatically from the constants obtained in noble gas matrix experiments. The vibrational spacings reported in Ref. 15 differ greatly from the vibrational spacing of the gas phase experiments.

VI. SUMMARY

MgCa molecules have been generated and identified in the gas phase for the first time. The MgCa molecules have been produced in a concentric heat pipe oven and investigated by the method of laser induced fluorescence.

Using several ion laser lines between 454.5 and 568.2 nm and using a tunable, stabilized, single mode dye laser in the range from 574 to 592 nm discrete fluorescence spectra were taken and analyzed. In case of the X state the IPA procedure was applied to obtain the correct assignment of the quantum numbers v'', J'', and J'. The vibrational quantum numbers v' of the excited A, B, and C states were determined by a comparison of the photoelectrically measured line intensities and the calculated Franck–Condon factors which are in very good agreement. The molecular constants of the different electronic states are tabulated and the IPA potential energy curve of the ground state is given.

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[33] See AIP document no. PAPS JCPSA-82-3491-32 for 32 pages containing the measured line positions of the MgCa molecule. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages, and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.