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High-resolution spectrum of the $B\,^4\Sigma_u^-$-$X\,^4\Sigma_g^-$ electronic system of C_2^+ using fast-ion beam-laser spectroscopy

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In this work, we present a more highly resolved spectrum of the transitions of C_2^+. To avoid the difficulty of the observation of the $B\,^4\Sigma_u^-$-$X\,^4\Sigma_g^-$ emission spectrum of C_2^+ by conventional methods, we used a technique based on fast-ion-beam laser spectroscopy which presents a very-high-resolution performance (120 MHz or less). Spin-spin and spin-rotation coupling parameters have been determined for the first time for both involved states.

The laser-induced fluorescence spectrum of C_2^+ was recently observed by Maier and co-workers[1,2] whereas the neutral species C_2 is well known, often observed, and easily produced. The possible emission range can be approximately obtained from *ab initio* calculations[3] which predicted the first electronic transitions to be in the 400–500-nm wavelength range, where the strong emission of C_2 has been observed.[4] In such a case, C_2^+ becomes a good example for fast-ion-beam laser spectroscopy combining laser and mass spectroscopy. By conventional emission spectroscopy, it was not possible to observe the emission spectrum of C_2^+ in the visible. By mass spectroscopy, C_2^+ can be isolated with great chemical purity and the work of O'Keefe, Derai, and Bowers[5] using translational energy spectroscopy led to an experimental observation of the electronic transitions. Now, using a mass selected beam of C_2^+ superimposed on a laser beam, it is possible to study under favorable conditions the rotational structure of its first electronic system. This experimental technique, named fast-ion-beam laser spectroscopy (FIBLAS), also has the advantage of using fixed laser lines and Doppler scanning.

Doppler-tuned laser spectroscopy on an ion beam has been extensively described many times.[6,7] The C_2^+ ions were produced in a low-voltage discharge source using a mixture of acetylene and helium. After acceleration to energies in the range of 40–90 keV, C_2^+ ions were mass selected by magnetic deflection and made collinear with a counter-propagating light beam of a single-mode cw Ar^+ laser. The typical current downstream was of the order of 100 nA. Doppler tuning was obtained by postaccelerating C_2^+ ions in an electrically insulated region to which a variable voltage was applied. The lifetime[2] of the excited level being 127 ns, the fluorescence induced by the resonant laser light at 4727 Å was observed about 10 cm down from the entrance of the postaccelerating region. The fluorescence light, collected by a lens, was detected from the (1-1) band by a cooled photomultiplier equipped with a narrow band-pass interference filter in order to suppress the background light arising from ion residual gas collisions and scattered laser light. Under these experimental conditions, the resonance signals were about as large as the background. Storing photocounts and sweeping the postaccelerating voltage were carried out simultaneously by a minicomputer. A typical spectrum is shown in Fig. 1. The width of the resonance peaks, of the order of 120 MHz, was due to energy spread in the ion source, ripple of accelerating voltage, and laser jitter. The accelerating voltage was measured with a relative uncertainty of 3×10^{-4} by means of a high-voltage resistive divider which had been calibrated during laser spectroscopy experiments on fast neutral atomic beams obtained from an ion beam by charge transfer.[8] Knowing that the energy of ions extracted from the source depended on source parameters and that the laser frequency could change, we have estimated the absolute uncertainty in the wave numbers of resonance peaks at 0.02 cm^{-1}.

In this work, only P branches have been investigated, the R branches being outside of our spectral range. The high-resolution spectrum of the band-head region of the (1-0) band of the $B\,^4\Sigma_u^-$-$X\,^4\Sigma_g^-$ system of C_2^+ is shown in Fig. 1. The observed rotational lines are given in Table I. Even with our resolution, some of the lines are not resolved and make the rotational analysis difficult. The spectrum shows more than the expected four P branches related to a $^4\Sigma$-$^4\Sigma$ transition if we consider their line strengths given by Kovacs.[9] In fact, we observe patterns of two, three, and four components for the different values of the rotational quantum number N. After detailed investigation we have been able to explain this feature of the spectrum. We found that the spin-spin coupling and the spin-rotation coupling are nearly identical for the two states involved in that transition. That explains the observed behavior of the spectrum because for both electronic states the F_3 and F_4 (corresponding to $N=J+\frac{1}{2}$ and $N=J+\frac{3}{2}$, respectively) components are equally separated for a given low value of N, as are also the F_1 and F_2 (corresponding to $N=J-\frac{3}{2}$ and $N=J-\frac{1}{2}$) components. These separations change with high value of the rotational quantum number N. That means that for values of $N\leq 11$ we observe only two components, and for $N\geq 13$, only the F_1-F_2 separation becomes different for both states, so that three lines are observed [see line $P(13)$ in Fig. 1]. Finally, for $N\geq 15$, both the F_1-F_2 and F_3-F_4

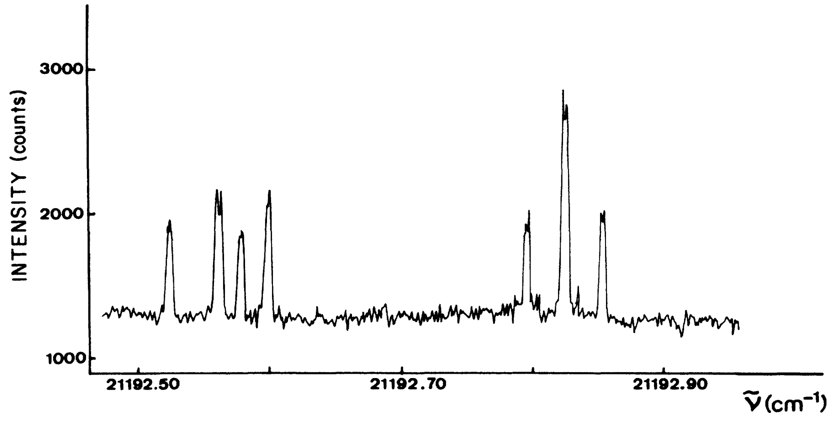

FIG. 1. High-resolution fluorescence spectrum of the band-head region of the (1-0) band of the $B\,^4\Sigma_u^- - X\,^4\Sigma_g^-$ system of C_2^+. By increasing wave number, we show the four spin components of the $P(15)$ rotational lines and the not complete resolved pattern of the $P(13)$ for which the P_3 and P_4 spin components are overlapped. This spectrum was obtained for a Doppler scan of 1 kV.

separations are different in the two electronic states, and four rotational components are observed [see line $P(15)$ in Fig. 1]. Our rotational assignments are in agreement with the results of Maier and Rosslein[2] obtained by Doppler-limited laser spectroscopy. It seems that a very small splitting is observed for each individual line and does not change with the rotational quantum number N. This structure cannot be explained by an additional fine or hyperfine effect (^{12}C has a zero nuclear spin). This effect is probably due to an experimental artifact, and at this time we do not have a reliable interpretation.

Although the energy formula for $^4\Sigma^-$ states has been discussed by various authors,[10-12] few $^4\Sigma^- - ^4\Sigma^-$ systems have been reported to date. The two states $^4\Sigma^-$ belong to the Hund's case coupling (b) and the purpose of this work is to analyze all its spin splitting components. Since C_2^+ is a homonuclear molecule composed of nuclei with zero nuclear spin, the even values of N levels of the ground state and the odd ones for the excited state, which both have negative parity, are missing. In the present work, we used the $^4\Sigma$ Hamiltonian from Albritton *et al.*[12] for the rotational analysis of the spectrum. The centrifugal distortion terms of higher order are also readily added. A term value approach and the nonlinear least-squares method have been used to determine upper- and lower-state constants from wave numbers of the rotational lines. All the lines were weighted by unity. A very satisfactory fit was achieved, the overall standard deviation being 0.04 cm^{-1}, with no level giving a residual of more than 0.07 cm^{-1}. The final constants are given in Table II. Since only the P lines were observed, the mean rotational constants B_v, D_v, and γ_v in both states are correlated. However, the obtained values for the B_v constants are in good agreement with those determined by Maier and Rosslein.[2] To confirm the determination of the γ_v spin-rotation constants, we developed a specific procedure. We fixed the value of the ground state to different values between 0 and 4 cm^{-1} and by step determined the corresponding one for the upper state. Consequently, the given values of Table II correspond to the minimum of the standard deviation obtained previously. The large values of these γ_v constants reveal a perturbation in both electronic states caused by spin-orbit interaction. From Fig. 2, we see that several quartet states can contribute to the spin-orbit interaction. As a perturbing state, there is also the $2\,^2\Pi_u$ state as suggested by Maier and Rosslein. Further

TABLE I. Wave numbers (cm^{-1}) of the observed rotational lines. o−c stands for observed minus the calculated values.

	P_1		P_2		P_3		P_4	
N	obs.	o−c	obs.	o−c	obs.	o−c	obs.	o−c
7	21 197.547[a]	0.031	21 197.547[a]	0.042	21 197.495[a]	0.021	21 197.495[a]	0.054
9	195.039[a]	0.011	195.039[a]	0.010	194.996[a]	0.015	194.996[a]	0.015
11	193.484[a]	0.021	193.484[a]	0.032	193.375[a]	0.031	193.375[a]	0.032
13	192.855	0.042	192.798	0.077	192.826[a]	0.061	192.826[a]	0.067
15	192.599	−0.052	192.577	−0.046	192.546	−0.041	192.524	−0.071
17	193.717	0.071	193.705	0.040	193.640	0.065	193.607	0.055
19	195.331	−0.001	195.310	0.023	195.269	0.031	195.215	−0.021
21	197.888	0.023	197.817	0.008	197.760	−0.034	197.713	−0.049

[a] Denotes blended line.

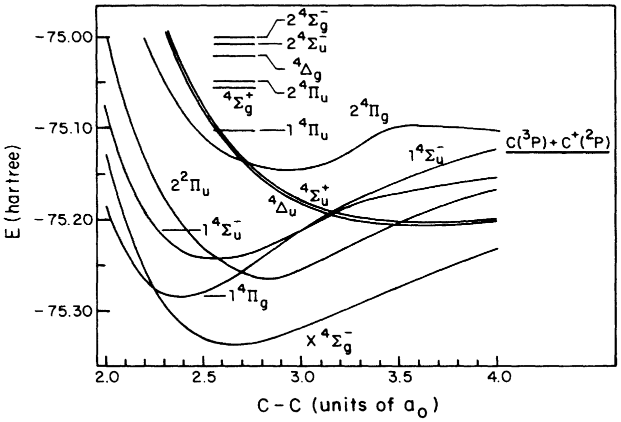

FIG. 2. Potential curves of some molecular states in the C_2^+ system with those relevant in this work. These curves were taken from Ref. 3.

analysis of this perturbation by including higher-order spin-orbit effects are in progress.

In conclusion, we present a high-resolution spectrum of the $B\,^4\Sigma_u^-$-$X\,^4\Sigma_g^-$ transitions of the C_2^+ ion obtained by FIBLAS. We have been able to analyze the split rotational lines and have derived the spin-spin, ϵ_v, and spin-rotation, γ_v, coupling parameters for both states. However, the values of the spin-rotation parameters should be taken with care because it is found that a strong spin-orbit perturbation probably occurs in the two states and possibly contaminates the γ_v parameters. Further studies are in progress to understand this perturbation. This work gives some insight into the complex rotational structure of the C_2^+ ion in its first electronic system.

TABLE II. Molecular constants of the C_2^+ $X\,^4\Sigma_g^-$ ($v''=0$) and $B\,^4\Sigma_u^-$ ($v'=1$) states (cm^{-1}). The number in parentheses corresponds to one standard deviation expressed in terms of the last digits.

	T_v	B_v	$10^6 D_v$	ϵ_v	γ_v
$X\,^4\Sigma_g^-$ ($v''=0$)	0.0	1.4176(3)	6.3(5)	−0.944(7)	2.794(5)
$B\,^4\Sigma_u^-$ ($v'=1$)	21 213.58(5)	1.5224(1)	5.8(2)	−0.952(8)	3.021(1)

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