

LASER INDUCED FLUORESCENCE FROM CF₂ EXCITED AT 248 nm

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KrF-laser-induced fluorescence from CF₂-radicals was investigated during photolysis of CF₂Cl₂ and CF₂HCl by 193 nm laserlight. In contrast to other publications, which postulated single-vibronic-level fluorescence, the fluorescence is caused by excitation from four closely situated absorption bands. These fluorescence bands of four series, are assigned to $\tilde{A}^1B_1(v'_1, 6 - 2v'_1, 0) - \tilde{X}^1A_1(v''_1, v''_2, 0)$ transitions with $\Delta v_1 = 0$ and $0 \leq v''_2 \leq 30$. The Franck-Condon factors of the $\tilde{A}^1B_1(0, 6, 0) - \tilde{X}^1A_1(0, v''_2, 0)$ transitions, the frequencies of the bending vibration ($\omega''_2 = 673 \pm 2 \text{ cm}^{-1}$) and the anharmonicity constants $x''_{22} = -0.94 \pm 0.08 \text{ cm}^{-1}$ and $x''_{22} = -0.44 \pm 0.10 \text{ cm}^{-1}$ were more precisely determined. For the first time higher anharmonicity constants are evaluated with $x''_{12} + x''_{112} = -3.5 \pm 1.0 \text{ cm}^{-1}$ and $x''_{122} = -0.05 \pm 0.02 \text{ cm}^{-1}$.

KEY WORDS: Photolysis, laser-induced fluorescence, difluoromethylene, uv-spectrum.

INTRODUCTION

Difluoromethylene radicals are formed by dissociation of fluorosubstituted hydrocarbons in atmospheric sunlight photolysis, multiphoton processes, electrical discharges and plasmachemical structuring of polymers.^{1,2}

Though the chemical properties of these radicals were studied in many investigations, knowledge about their molecular parameters, their large absorption, and emission spectra, is still incomplete. This applies especially to the detection of CF₂-radicals by resonant laser-induced excitation of the $\tilde{A}^1B_1(0, 6, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition† by KrF excimer lasers at 248 nm, which produces fluorescence of CF₂ between 248 and 450 nm.^{3,4}

The aim of this work is to give a more extended interpretation of the KrF-laser-induced fluorescence of the CF₂-radicals. The single-vibronic-level (SVL) fluorescence of CF₂ postulated in recent publications^{5,6} is discussed on the basis of measured data in comparison with recent published data. Part of the molecular parameters and the Franck-Condon factors are determined anew or for the first time according to the new classification of the fluorescence bands, respectively.

The molecular constants of CF₂ from the literature and this work are shown in Table 1.

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† In the following the electronic CF₂-levels are labelled for simplicity by their first letter only.

Table 1 Molecular constants of CF₂ in cm⁻¹

Ref.	[7]	[3]	[5]	[8]	[9, 11]	[10]	This work
Medium	gas	gas	gas	gas	gas	matrix	gas
Method	absor.	LIF	LIF	emiss.	FT-IR	absor.	LIF
ν_{00}	37226		37197	37197			37215
ω_1'	1223		1186		1225, 0796	1222	
ω_2''	665	672	666	663	≈670	668	673
ω_3''	1102				1114, 4435	1102	
ω_1'	1017		976				
ω_2'	496		497	491.4			499
x_{22}'				0.52			-0.44
x_{22}''		-1.1		-0.50			-0.94

Matthews *et al.* investigated the UV-spectrum of CF₂ in absorption.⁷ They analysed some bands with resolved rotational structure at a temperature of 173 K. Besides the very intense $\tilde{A}(0, \nu_2', 0) - \tilde{X}(0, 0, 0)$ bands the $\tilde{A}(1, 4, 0) - \tilde{X}(0, 0, 0)$ and $\tilde{A}(1, 5, 0) - \tilde{X}(0, 0, 0)$ transitions were observed, which nearly coincided with the $\tilde{A}(0, 6, 0) - \tilde{X}(0, 0, 0)$ and $\tilde{A}(0, 7, 0) - \tilde{X}(0, 0, 0)$ bands.

King, Schenck and Stephenson⁵ analysed the UV-spectrum by laser-induced fluorescence (LIF) with various excitation wavelengths. The low resolution of the dispersed fluorescence spectra caused relatively large errors in the determination of the wavenumbers of the intensity maxima of the bands and this had consequences for their classification. As a result of these facts, all observed laser-induced fluorescence spectra were interpreted as SVL-fluorescence exclusively.^{6,17}

EXPERIMENTAL

CF₂-radicals were prepared by photolysis of CF₂Cl₂ at 193 nm in a stainless steel cell with quartz windows, and the ArF- and KrF-excimer laser penetrated the photolysis cell unfocussed, collinearly in opposite directions with a cross-section of 2 cm². The dispersed fluorescence was measured perpendicularly to the laser beams by a prism monochromator (SPM 12 CZ-Jena) and photomultiplier. Attainable resolution depended on the wavelength and varied in the range from 0.05 nm at 250 nm to 0.4 nm at 400 nm.

Spectral sensitivity calibration of the detection system was achieved by means of deuterium and tungsten-ribbon lamps. Mean energies of excimer laser pulses were 100 mJ (ArF, 16 ns) and 200 mJ (KrF, 26 ns). The delay between the two laser pulses was held constant at 6 ms, and the pressure inside the photolysis cell could be varied in the range from 1 to 1000 Pa. The KrF-laser induced spectra were measured at a pressure of 200 Pa to avoid errors in the wavelength determination of band maxima by nonthermal population of the rotational states in the excited vibronic level. At this pressure the collisionally induced excitation of additional fluorescence bands is negligible, as the absence of characteristic bands, e.g. $\tilde{A}(0, 5, 0) - \tilde{X}(0, 0, 0)$, shows.

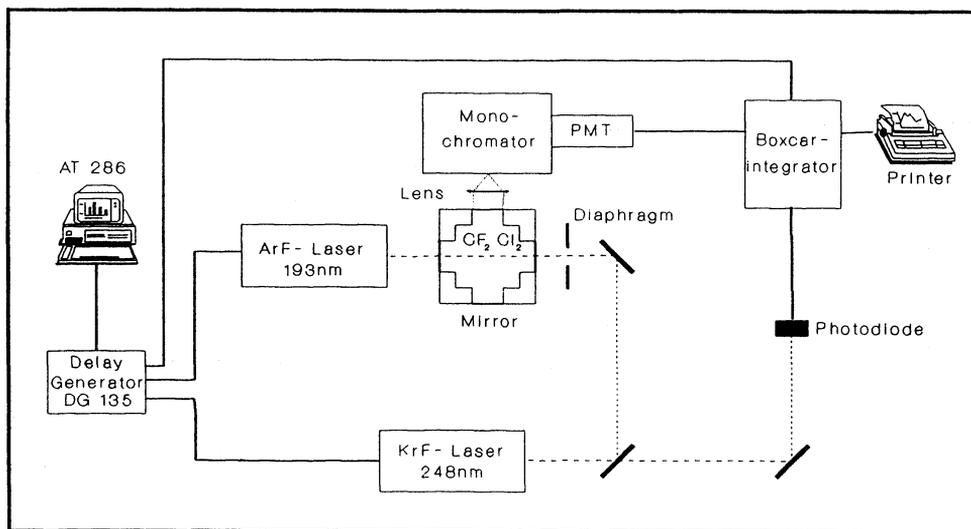


Figure 1 Experimental scheme.

RESULTS AND DISCUSSION

In the wavelength range of the KrF-laser (248.4 nm and FWHH = 0.36 nm) the CF_2 -radical has some absorption bands of the $\tilde{A}^1B_1 - \tilde{X}^1A_1$ -transition. The $\tilde{A}(0, 6, 0) - \tilde{X}(0, 0, 0)$ band has the highest absorption coefficient. Figure 2 shows the characteristic form of this band, as it was calculated with data of Ishiguro *et al.*⁸ at a temperature of 300 K and according to the resolution of the applied monochromator.

The full width at half height of that absorption band is 60 cm^{-1} under these conditions. As can be seen, the absorption coefficient diminishes to higher wavenumber more slowly than to the other side. Because the maximum of this absorption band does not coincide with the center of KrF-laser line, mainly rotational states with $k = 3$ to 5 are populated by absorption of these photons. This situation is observed in pressure-dependent dispersed LIF-spectra in the vicinity of the excitation wavelength (Figure 3).

We note that for higher pressures the intensity maximum of the $\tilde{A}(0, 6, 0) - \tilde{X}(0, 0, 0)$ fluorescence band at 40183 cm^{-1} grows in relation to the fluorescence close to the KrF-laser line. This dependence is explained by the growing collisional relaxation during the fluorescence lifetime (55 ns), which intensifies the emission in the fluorescence band maximum. In the spectral width of the KrF-laser there exist further possible absorption bands, such as $\tilde{A}(1, 4, 0) - \tilde{X}(0, 0, 0)$ at 40211 cm^{-1} , $\tilde{A}(2, 2, 0) - \tilde{X}(0, 0, 0)$ at 40235 cm^{-1} and $\tilde{A}(3, 0, 0) - \tilde{X}(0, 0, 0)$ at 40256 cm^{-1} . The Franck-Condon factors of these transitions decrease with increasing Δv_1 . Especially the transitions with $\Delta v_1 = 2$ and 3 coincide very well with the broad intensity maximum of KrF laser emission at 40246 cm^{-1} . Absorption wavelengths

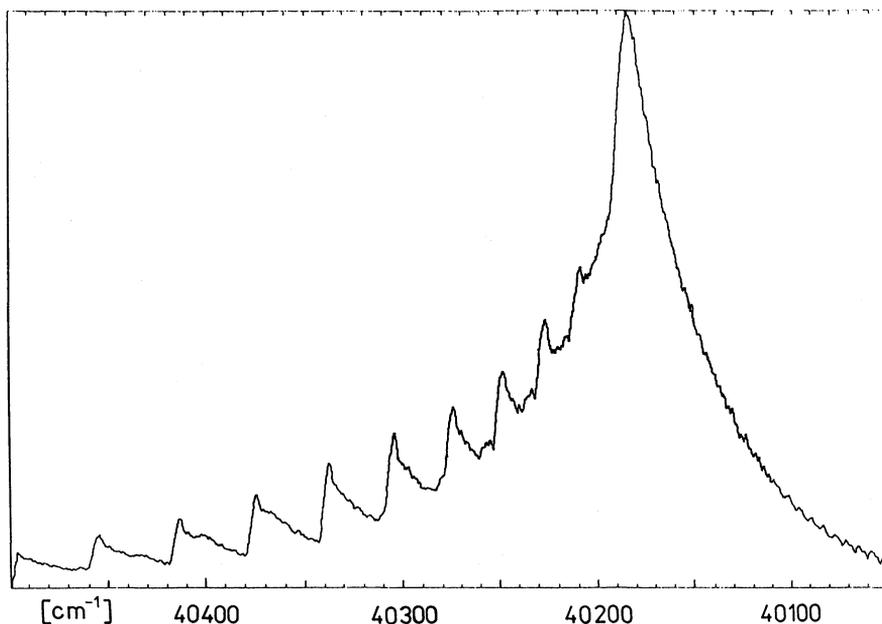


Figure 2 Calculated $\tilde{A}(0, 6, 0) - \tilde{X}(0, 0, 0)$ absorption band of CF_2 .

of bands with $\nu_3 > 0$ are not known, because there is no information about the value of ω_3 in the excited state.

The observed and spectrally corrected (measured wavelengths were converted into vacuum wavelengths) dispersed KrF-LIF-spectrum of CF_2 is shown in Figure 4.

This spectrum is formed by four series of nearly equidistant fluorescence bands (see also Ref. 17). The most intense one is assigned in accordance with Sam and Yardley³ as the $\tilde{A}(0, 6, 0) - \tilde{X}(0, \nu_2', 0)$ series. As shown in the expanded part of the spectrum at 300 nm (Figure 5), up to three additional bands are seen on the short wavelength side of each of these bands in a distance of approximately 140 cm^{-1} . In some cases, these fluorescence bands are more intense than the bands of the $\tilde{A}(0, 6, 0) - \tilde{X}(0, \nu_2', 0)$ series (see e.g. Figure 4, $\nu_2' = 6, 7, 10, 14, 18, 19$).

There are two possibilities to assign the additional bands.

1. These bands are transitions of $\tilde{A}(0, 6, 0) - \tilde{X}(\nu_1', \nu_2', 0)$ type with $\nu_1' = 1, 2, 3$ according to the SVL-fluorescence postulated by King *et al.*
2. These bands are transitions with $\Delta\nu_1 = 0$ and of the following type: $\tilde{A}(\nu_1', 6 - 2\nu_1', 0) - \tilde{X}(\nu_1', \nu_2', 0)$ with $\nu_1' = \nu_1'' = 1, 2, 3$.

The observed distance D_1 of the $\tilde{A}(0, 6, 0) - \tilde{X}(0, \nu_2', 0)$ bands to the first adjacent band is shown in Figure 6. For $\nu_2' < 10$ this distance is measured as $D_1 = 138 \pm 8 \text{ cm}^{-1}$. In the first case the calculated value of D_1 is

$$D_1 = [\tilde{A}(0, 6, 0) - \tilde{X}(1, \nu_2' - 2, 0)] - [\tilde{A}(0, 6, 0) - \tilde{X}(0, \nu_2', 0)]$$

$$D_1 = 2\omega_2'' + 4x_2'' - \omega_1' = 115 \text{ cm}^{-1}$$

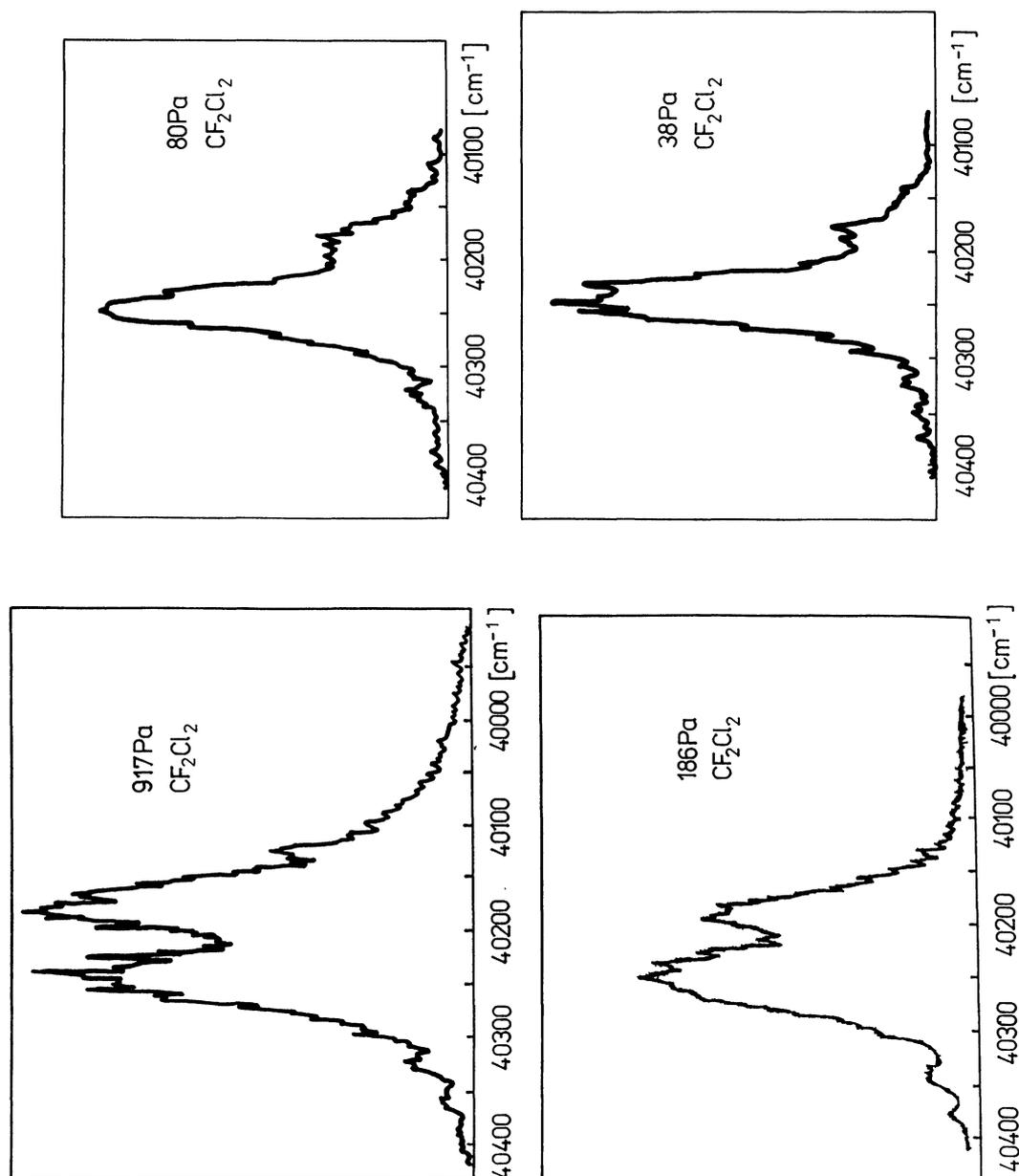


Figure 3 Pressure dependent LIF-spectra of CF_2 near the excitation laser line at 248 nm.

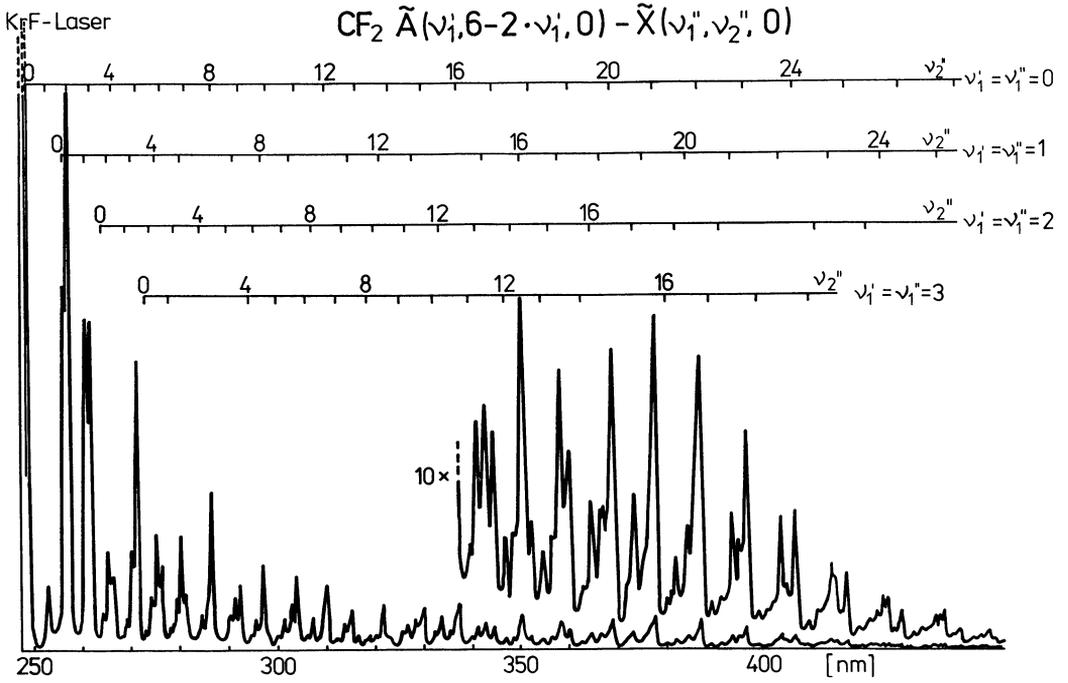


Figure 4 Dispersed KrF-LIF spectrum of CF_2 -radicals with new assignment of bands.

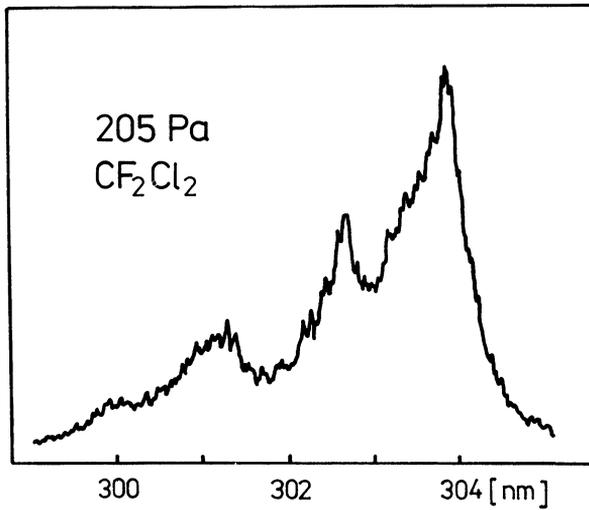


Figure 5 Expanded part of the CF_2 -spectrum at 300 nm.

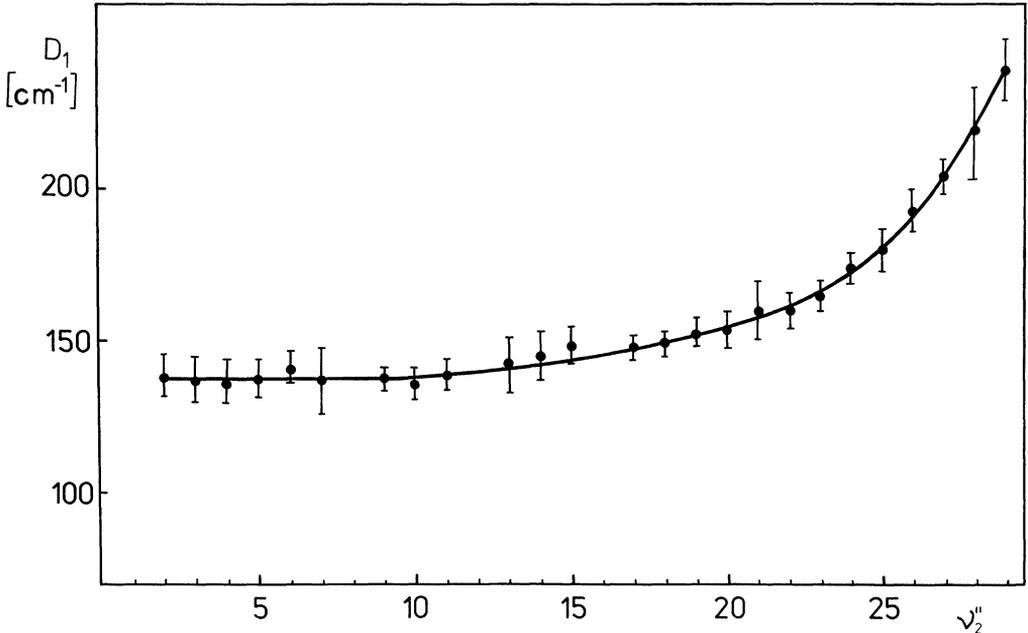


Figure 6 Distance of $\tilde{A}(0, 6, 0) - \tilde{X}(0, v_2'', 0)$ transitions to the adjacent band vs. v_2'' .

according to SVL-fluorescence with the data of Refs. 3, 9. The measured distance for D_1 is obviously in contradiction to this calculated value.

The only possible conclusion left is that the absorption of KrF-laser photon is not a SVL-process. In this case the first adjacent bands are assumed to be $\tilde{A}(1, 4, 0) - \tilde{X}(1, v_2'' - 2, 0)$ transitions, and D_1 becomes

$$D_1 = [\tilde{A}(1, 4, 0) - \tilde{X}(1, v_2'' - 2, 0)] - [\tilde{A}(0, 6, 0) - \tilde{X}(0, v_2'', 0)].$$

Taking into account that the distance between the $\tilde{A}(0, 6, 0) - \tilde{X}(0, 0, 0)$ band and $\tilde{A}(1, 4, 0) - \tilde{X}(0, 0, 0)$ band is $\leq 24 \text{ cm}^{-1}$,⁷ D_1 becomes $\leq 139 \text{ cm}^{-1}$. Neglecting the anharmonicity in the excited state ($\omega_1' - 2\omega_2' = 25 \text{ cm}^{-1}$ (Ref. 7)) D_1 is evaluated to be 140 cm^{-1} . Because of the good coincidence with the measured value of D_1 , it is concluded that the first adjacent additional bands are $\tilde{A}(1, 4, 0) - \tilde{X}(1, v_2'', 0)$ transitions.

Applying this method also to the second and third band series, they are assigned as $\tilde{A}(2, 2, 0) - \tilde{X}(2, v_2'', 0)$ and $\tilde{A}(3, 0, 0) - \tilde{X}(3, v_2'', 0)$ transitions. Obviously, four excited electronic states $\tilde{A}(v_1', v_2', 0)$ with $v_1' = 0, 1, 2, 3$ and $v_2' = 6 - 2v_1'$ are populated in CF_2 by the absorption of KrF-laser photons.

It is necessary to point out that the decrease of Franck-Condon factors for higher Δv_1 in absorption is partially compensated by higher laser intensity in the range of absorption maxima of these bands. As absorption bands with $\Delta v_1 = 0, (v_2)$ and $\Delta v_1 = 1, (v_2 - 2)$ have a distance of $\approx 25 \text{ cm}^{-1}$ only, non-SVL excitation is possible at other excitation wavelengths and by sources with smaller bandwidth too. For

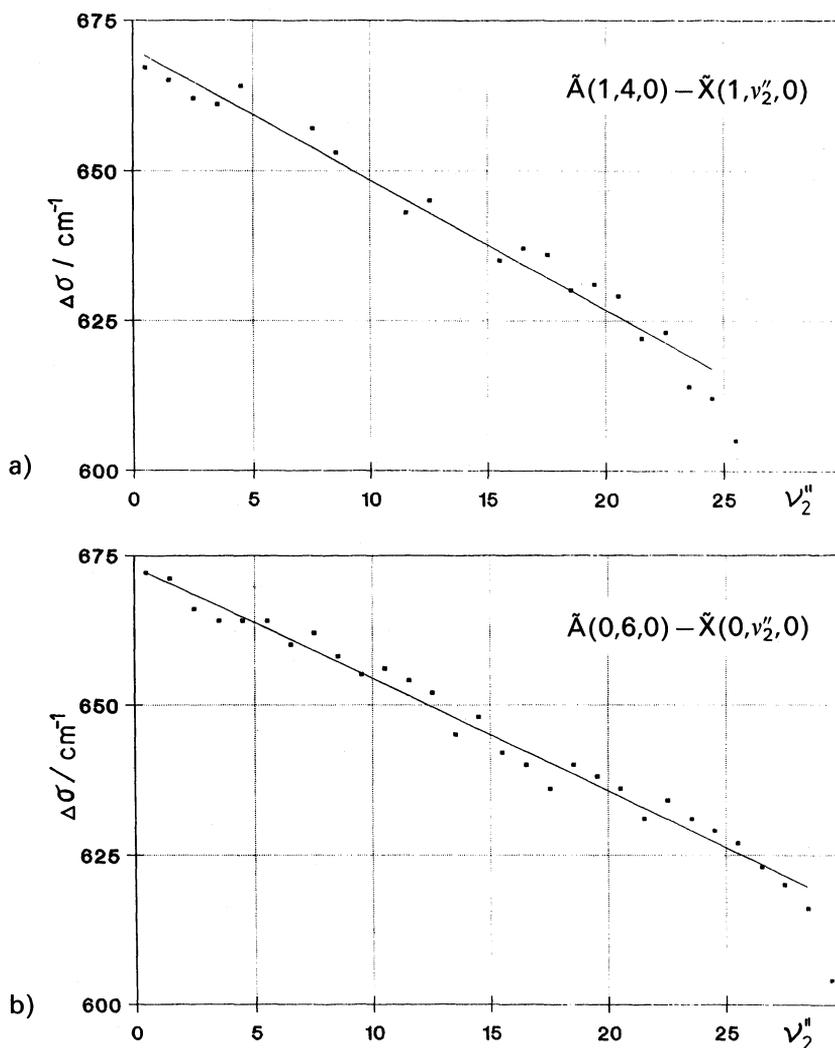


Figure 7 Birge-Sponer diagrams. (a) For $\tilde{A}(0,6,0) - \tilde{X}(0,\nu_2'',0)$ series; (b) for $\tilde{A}(1,4,0) - \tilde{X}(1,\nu_2'',0)$ series.

further studies it is suggested to investigate which vibronic levels are populated by excitation at other wavelengths.

The wavenumbers of the maxima of all observed bands are given in a Deslandres table (Table 2). A graphical representation of the first differences in wavenumbers of adjacent bands in dependence on the quantum number ν_2 in the series (Birge-Sponer diagram = BSD) is shown in Figure 7. The dependence is well approximated by a straight line and we may assume that higher anharmonicity terms can be neglected. The linear regression of the $\text{BSD}_0(\nu_2'')$ gives the anharmonicity constant by slope

$x''_{22} = -0.94 \pm 0.08 \text{ cm}^{-1}$ and the frequency of bending vibration $\omega''_2 = 673 \pm 2 \text{ cm}^{-1}$ by the ordinate intersection point.

The molecular constants of the excited state were determined from $\text{BSD}_0(v''_2)$ using the measured wavenumber of the $\tilde{A}(0, 6, 0) - \tilde{X}(0, 0, 0)$ band and literature data^{5,7,8,15} of other $\tilde{A}(0, v''_2, 0) - \tilde{X}(0, 0, 0)$ transitions. From BSD we found $\omega''_2 = 499 \pm 3 \text{ cm}^{-1}$ and $x''_{22} = 0.44 \pm 0.10 \text{ cm}^{-1}$. The wavenumber of the $\tilde{A}(0, 0, 0) - \tilde{X}(0, 0, 0)$ band is calculated from $\tilde{A}(0, 6, 0) - \tilde{X}(0, 0, 0)$ band maximum wavenumber by subtracting the vibrational energy in the excited state to be 37205 cm^{-1} . The origin of the $\tilde{A}(0, 0, 0) - \tilde{X}(0, 0, 0)$ band however is at 37215 cm^{-1} , because in the modeled $\tilde{A}(0, 6, 0) - \tilde{X}(0, 0, 0)$ fluorescence band the distance of the band maximum to the origin is 10 cm^{-1} .

As Figure 6 shows, the distance of the $\tilde{A}(0, 6, 0) - \tilde{X}(0, v''_2, 0)$ bands to the $\tilde{A}(1, 4, 0) - \tilde{X}(1, v''_2 - 2, 0)$ bands grows nonlinearly with v_2 . How could this be explained?

The vibrational energy levels of triatomic molecules are given¹⁶ in reduced form by

$$w_i = \omega_i + x_{ii} + \sum_{i \neq k} \frac{x_{ik}}{2}$$

$$G_0(v_1, v_2, 0) = w_1 v_1 + x_{11} v_1^2 + x_{111} v_1^3 + x_{12} v_1 v_2$$

$$+ x_{112} v_1^2 v_2 + w_2 v_2 + x_{22} v_2^2 + x_{222} v_2^3 + x_{122} v_1 v_2^2$$

assuming that the asymmetric stretch vibration is not excited. The position of the vibronic transition is then

$$\sigma(v'_1, v'_2, v''_1, v''_2) = \nu_{00} + G_0(v'_1, v'_2, 0) - G_0(v''_1, v''_2, 0).$$

The distance of adjoining bands is then

$$D_1 = [\tilde{A}(1, 4, 0) - \tilde{X}(1, v''_2 - 2, 0)] - [\tilde{A}(0, 6, 0) - \tilde{X}(0, v''_2, 0)]$$

$$= w'_1 + x'_{11} + x'_{111} - w''_1 - x''_{11} - x''_{111} - 2w'_2 - 20x'_{22} - 152x''_{222}$$

$$+ 4x'_{12} + 16x'_{122} + 4x'_{112} + 2w''_2 + (4v''_2 - 4)x''_{22} - (v''_2 - 2)x''_{12}$$

$$+ (6v''_2{}^2 - 12v''_2 + 8)x''_{222} - (v''_2{}^2 - 4v''_2 + 4)x''_{122} - (v''_2 - 2)x''_{112}.$$

If $G_0(v'_1, v'_2, 0)$ is only quadratically approximated by v_1 , then $D_1(v''_2)$ becomes a straight line. If cubic terms in v_1 are taken into account, it is obvious that the nonlinearity of $D_1(v''_2)$ is connected with $(6x''_{222} - x'_{122})$.

The anharmonicity constant x''_{222} is negligibly small, because the $\text{BSD}_0(v''_2)$ of the $\tilde{A}(0, 6, 0) - \tilde{X}(0, v''_2, 0)$ transitions is observed to be linear up to $v''_2 = 28$ and

$$\text{BSD}_0(v''_2) = w''_2 + 2x''_{22}x''_{22} + 3x''_{222}v''_2{}^2$$

holds. As a result of this, we can say that nonlinear behavior of $D_1(v''_2)$ is mainly caused by x''_{122} . By regression from Figure 6 follows $x''_{122} = -0.05 \pm 0.02 \text{ cm}^{-1}$ assuming $x''_{222} = 0$.

The Birge-Sponer diagram $\text{BSD}_1(v''_2)$ of the $\tilde{A}(1, 4, 0) - \tilde{X}(1, v''_2, 0)$ transitions

Table 3 Frank-Condon factors (FCF) for the $\tilde{A}(0, 6, 0) - \tilde{X}(0, v_2'', 0)$ transitions of CF_2

v_2''	FCF	v_2''	FCF	v_2''	FCF
0	0.4780	11	0.0178	22	0.0071
1	0.0160	12	0.0156	23	0.0053
2	0.1340	13	0.0041	24	0.0033
3	0.0800	14	0.0032	25	0.0018
4	0.0180	15	0.0096	26	0.0009
5	0.0750	16	0.0113	27	0.0005
6	0.0211	17	0.0053	28	0.0002
7	0.0139	18	0.0031	29	0.0002
8	0.0384	19	0.0048	30	0.0001
9	0.0163	20	0.0073		
10	0.0051	21	0.0081		

gives,

$$BSD_1(v_2'') = w_2'' + 2x_{22}''v_2'' + 3x_{222}''v_2''^2 + x_{12}'' + 2x_{122}''v_2'' + x_{112}''.$$

Comparing BSD_0 and BSD_1 , it is stated that the intersection point lowers by $|x_{12}'' + x_{112}''|$ and the negative slope increases by $2x_{122}''$.

This tendency continues for $BSD_2(v_2'')$ of the $\tilde{A}(2, 2, 0) - \tilde{X}(2, v_2'', 0)$ fluorescence bands and one gets

$$BSD_2(v_2'') = w_2'' + 2x_{22}''v_2'' + 3x_{222}''v_2''^2 + 2x_{12}'' + 4x_{122}''v_2'' + 4x_{112}''.$$

From the slope of the linear regression of the ordinate intersection points of BSD 's over v_1 it follows $x_{12}'' + x_{112}'' = -3.5 \pm 1 \text{ cm}^{-1}$. An additional proof of the value of x_{122}'' is given by the decrease of slope of the BSD 's with v_1 .

Taking into account the errors in wavenumber determination and the limited range of fluorescence transitions, it is commendable to finish here the evaluation of anharmonicity constants.

The integral intensity of the fluorescence bands emitted from the same laser excited level depends only on the Franck-Condon factors of these transitions. As only the very intense $\tilde{A}(0, 6, 0) - \tilde{X}(0, v_2'', 0)$ series is not much overlapped by adjacent bands, it was possible to determine their Franck-Condon factors (Table 3). These values were evaluated from the maximum intensity of each transition, assuming that the width of bands at half height is constant in the series. Comparison with Franck-Condon factors in Ref. 5 showed some differences.

Because of overlapping with adjacent bands or their weakness in the fluorescence spectrum, the Franck-Condon factors in the other series are not evaluated. Some qualitative impressions, however, can be obtained from the spectrum (Figure 4). The determination of these Franck-Condon factors and the investigation of further molecular constants of the CF_2 -radicals will be achieved by future measurements with variation of the excitation wavelength.

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