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Visible luminescence study of the infrared multiphoton dissociation of 2-chloroethenylsilane

M. Santos [a,*], L. Díaz [a], J.A. Torresano [a], J. Pola [b]

[a] *Instituto de Estructura de la Materia, C.S.I.C., Serrano 121, 28006 Madrid, Spain*
[b] *Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Czech Republic*

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Abstract

The infrared multiphoton dissociation of 2-chloroethenylsilane induced by a tunable CO_2 laser, under both collision-free and collisional conditions, results in an intense visible luminescence. Spectral analysis of this emission was carried out, and a broad, structureless band, centred at about 650 nm, was obtained. The intensity of this luminescence was studied in relation to multiphoton dissociation as a function of the gas pressure and the frequency and fluence of the laser beam. Lifetime measurements of the luminescence were performed for different pressures of the parent molecule, and the radiative decay time was found to be 480 ± 20 ns. The quenching rate of this emission by homogeneous collisions is $(1.44 \pm 0.08) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. The luminescence was assigned to decay from the ${}^1B_1$ electronic state to the ${}^1A_1$ ground state of silylene formed within the laser pulse. The detection of silylene supports the previously postulated reaction pathways in the infrared multiphoton dissociation of 2-chloroethenylsilane. It also suggests that, at high fluence conditions, the chloroethene elimination channel dominates the dissociation reaction. © 1997 Elsevier Science S.A.

Keywords: 2-Chloroethenylsilane; Infrared multiphoton dissociation; Visible luminescence

1. Introduction

The laser-induced photodecomposition of silicon compounds is a problem of current interest due to its potential role in the chemical vapour deposition of silicon-based films [1–4]. A knowledge of the decomposition mechanism and of the resulting intermediate species is essential in order to understand and control the properties of the films. These properties usually depend on the wavelength and fluence of laser irradiation and on the precursor pressure.

In recent papers, we have studied the photodecomposition of 2-chloroethenylsilane (CES) induced by UV laser irradiation [5] and infrared multiphoton dissociation (IRMPD) using one and two laser fields [6]. In these papers, the following decomposition pathways of CES have been established

$$H_3Si\text{–}CH{=}CHCl \rightarrow H_3SiC{\equiv}CH + HCl \quad (1)$$

$$H_3Si\text{–}CH{=}CHCl \rightarrow H_2C{=}CHCl + H_2Si{:} \quad (2)$$

$$H_3SiC{\equiv}CH \rightarrow HC{\equiv}CH + H_2Si{:} \quad (3)$$

For low fluence conditions, the analysis of the final products and deposits formed shows that the dominant dissociation reaction in the IRMPD of CES is dehydrochlorination (Eq. (1)), followed by the decomposition of ethynylsilane (Eq. (3)). This dissociation pathway is different from the predominant β-elimination into alkene and halosilane observed in similar compounds [7,8]. Some evidence was also found indicating that, for higher fluence conditions, the chloroethene elimination channel (Eq. (2)) is favoured.

The appearance of spontaneous collisionless luminescence in the visible or UV region is one of the most interesting effects caused by multiphoton excitation and dissociation of polyatomic molecules [9]. It was observed early in the history of IR laser photochemistry, and triggered the discovery of IRMPD [10]. Luminescence has been widely used to clarify dissociation pathways and to identify primary dissociation products [11,12].

This paper reports the spontaneous luminescence produced in the IRMPD of CES, both in the collisionless and collisional regimes. We have studied the spectral and time dependence of this luminescence, as well as its dependence on the frequency, temporal profile and fluence of the infrared beam and the total pressure in the absorption cell. The spontaneous emission is attributed to the excited SiH_2 intermediate formed

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[*] Corresponding author. Tel.: +34 1 5616800; fax: +34 1 5645557.

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in the dissociation process, which gives support to the IR laser-induced decomposition channels of CES postulated in previous papers. In addition, the nearly instantaneous formation of SiH_2 suggests that the chloroethene elimination channel is dominant.

2. Experimental details

A Lumonics K-103 TEA CO_2 laser was employed for the irradiation of the CES samples. It was equipped with frontal Ge multimode optics (35% reflection) and a rear diffraction grating with 135 lines mm^{-1} blazed at 10.6 μm. The laser was operated with either a mixture of CO_2, N_2 and He (8 : 8 : 84) or an N_2-free mixture (15 : 0 : 85) to obtain a pulse without a temporal tail. The irradiation was carried out using the 10R(28) line at 936.8 cm^{-1}, nearly coincident with the SiH_3 mode of CES [6]. The wavelength was checked with a 16-A spectrum analyser (Optical Eng. Co.). The laser pulse temporal profile was monitored with a photon drag detector (Rofin Sinar 7415). This temporal profile, at the above-mentioned line, consisted of a spike of 85 ns (full width at half-maximum (FWHM)) followed by a tail of approximately 3 μs, or a spike of 70 ns (FWHM) without a tail when an N_2-free mixture was used.

The photolysis experiments were performed under static conditions in a Pyrex cell (diameter, 4.5 cm; length, 10 cm) fitted with a pair of NaCl windows orthogonal to another pair of quartz windows which allowed a crossed configuration for the IR beam and emitted luminescence. The laser beam was focused at the centre of the reaction cell by a NaCl lens of 10 cm focal length. The laser fluence was calculated as the ratio of the pulse energy (measured with a Lumonics 20D pyroelectric detector) to the FWHM cross-sectional beam area (measured at the cell position with a Delta Development Mark IV pyroelectric array).

The sample pressure in the cell was measured with two (0–1 hPa and 0–10 hPa) MKS Baratron gauges; the leak rate of the entire gas handling vacuum system was less than 3.3 Pa h^{-1}.

The luminescence was monitored orthogonal to the laser beam. It was focused through a quartz lens (4 cm focal length) at the entrance slit of a 25 cm Jarrell Ash monochromator attached to a R928 Hamamatsu photomultiplier tube (Fig. 1). The spectral resolution of the system was 7 nm, and the characteristic spectral response of the complete system was determined using a previously calibrated Philips A123A lamp. The CO_2 laser pulse, picked up by the photon drag detector, triggered a Tektronix TDS 540 digital oscilloscope which was used to collect the signals and send them to a personal computer where they were averaged and analysed.

Each point was obtained by averaging over ten measurements. After these ten shots, the amount of newly formed product did not disturb the recorded signal. For each point, a fresh CES sample was used. The time between the IR pulses exceeded 1 min, which appeared to be long enough for the solid particles to settle and for the gaseous products to diffuse out of the reaction zone.

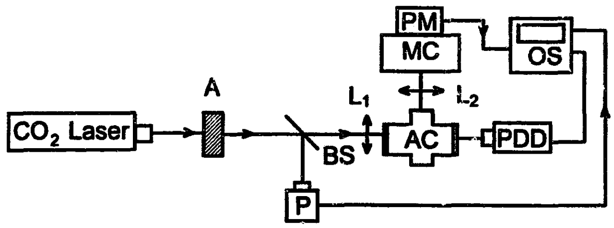

Fig. 1. Experimental set-up: A, attenuators; AC, absorption cell; BS, beam-splitter; MC, monochromator; L_1, NaCl lens; L_2, quartz lens; OS, oscilloscope; P, pyroelectric detector; PDD, photon drag detector; PM, photomultiplier.

CES was prepared following the chemical procedure given elsewhere [5].

3. Results and discussion

The irradiation of the CES molecule with a CO_2 laser beam tuned at 937 cm^{-1} gives an intense luminescence emission, which can be detected with the naked eye, for the entire range of pressures P and fluences ϕ used in the experiments: 0.1–1.0 hPa and 13–130 J cm^{-2} respectively. For the largest value of the fluence and for initial pressures higher than 1.5 hPa, the gas breakdown limit is achieved. We avoided these conditions in all the experiments.

The luminescence intensity depends significantly on the CO_2 laser wavelength. Fig. 2 shows the peak intensity of the signal at 650 nm, obtained from 0.3 hPa of CES, when the CO_2 laser wavelength is changed, keeping the energy of the laser pulses constant. As can be seen, the luminescence emission decreases strongly as the irradiation frequency is shifted from that resonant with the SiH_3 vibrational mode of CES. This indicates that the emission originates either from a multiphoton excitation process in the CES molecule, or by one or more excited fragments formed during dissociation.

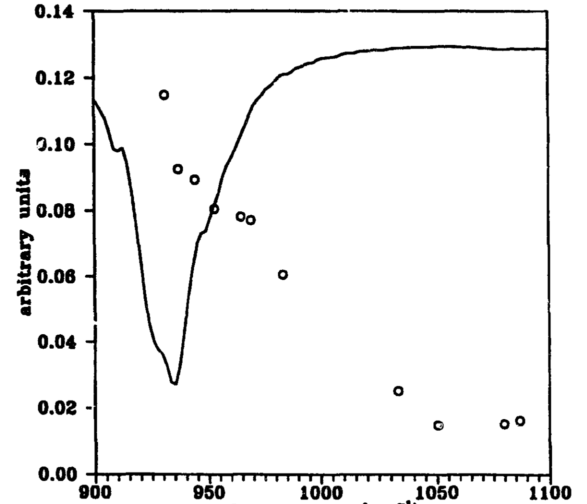

Fig. 2. Dependence of the luminescence peak intensity at 650 nm on the wavelength of the CO_2 laser pulse (O). P = 0.3 hPa, ϕ = 75 J cm^{-2}. The IR linear absorption spectrum is shown as reference (full line).

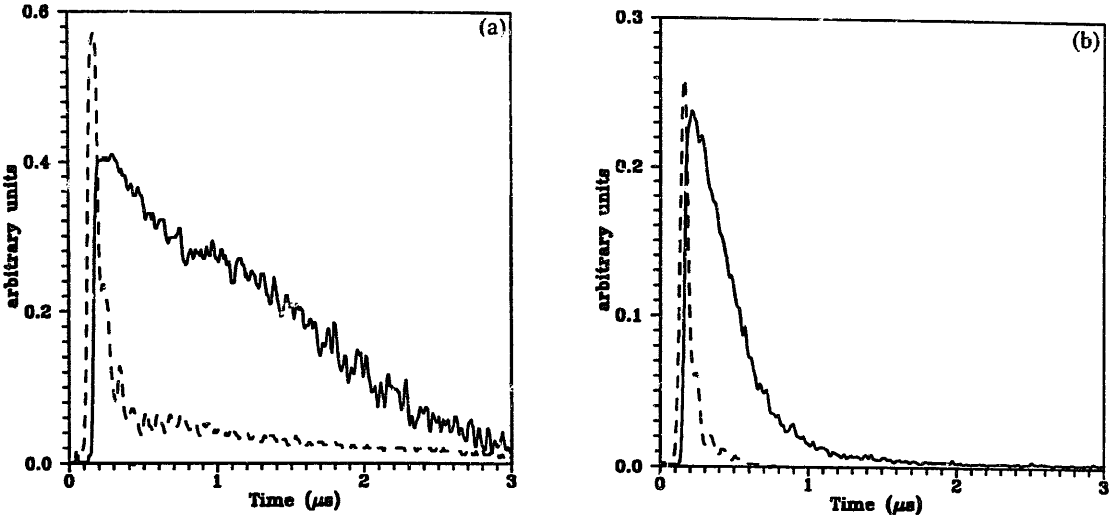

Fig. 3. Time profiles of the emission signals (full lines) induced by a pulse with a temporal tail (a) and a tail-free pulse (b). In both cases, the broken lines indicate the time profile of the CO_2 laser pulse.

Despite this rapid decay, a very low intensity signal is obtained when the irradiation frequency is as far as 146 cm^{-1} from the peak of the 934 cm^{-1} CES absorption band. This effect may be explained by considering the high absorption coefficient at the irradiated absorption band [6] and the high values of fluence employed in our experiments, for which large broadenings of the IR bands are expected.

Fig. 3 shows the temporal profiles of the luminescence recorded at 650 nm when 0.3 hPa of CES was irradiated by a tailed laser pulse of 106 J cm^{-2} (a) and by a tail-free pulse of 75 J cm^{-2} (b). The signal detected in the former case is much longer than that originating from the latter. Both signals appear a few nanoseconds (approximately 15 ns) before the infrared pulse reaches its maximum, with a risetime (approximately 40 ns) which follows the CO_2 pulse risetime. The long decay of the signal in Fig. 3(a) may be assigned to the contribution of multiphoton excitation and/or dissociation effects originating from the energy contained in the tail of the IR pulse [13]. All the experiments in this work, other than those shown in Fig. 2, were carried out with tail-free pulses.

In Fig. 4, we show the luminescence spectrum between 350 and 850 nm obtained by irradiating 0.5 hPa of CES with infrared pulses of 75 J cm^{-2}. The spectrum centred at about 650 nm is broad and structureless, indicating that many rovibronic levels are excited. These spectral features are typically found in luminescence emissions from the infrared multiphoton absorption and dissociation of a number of molecules [9]. Other reasons which may explain such a wide band structure include intermode coupling in the molecular quasi-continuum and inhomogeneous broadening of the luminescence spectrum due to the multiphoton excited population [13]. Throughout the studied spectral interval, the decay profiles of the signals can be fitted to a single exponential function. This confirms that one species is responsible for the emission, i.e. the parent molecule or a photoproduct.

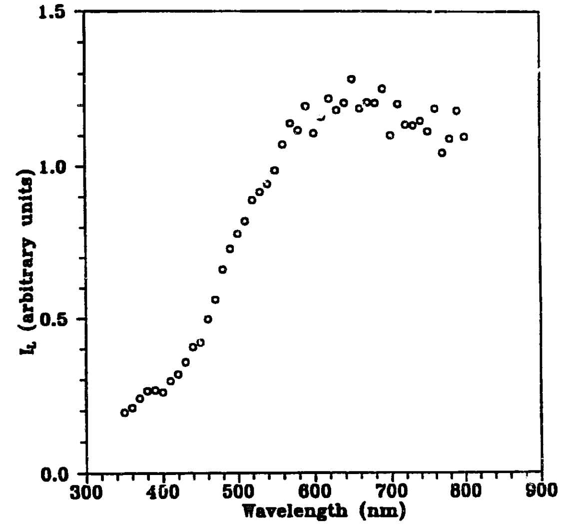

Fig. 4. Spectrum of the emission signal following the irradiation of 0.5 hPa of CES with infrared pulses of 75 J cm^{-2}.

The maximum intensity of the spontaneous luminescence at 650 nm is plotted as a function of the initial pressure in the cell in Fig. 5. A linear dependence is observed in the pressure range 0.1–0.6 hPa, indicating that, within this interval, the luminescence stems from a collisionless process. For pressures higher than approximately 0.6 hPa, the slope of the linear dependence decreases, suggesting pressure quenching of the luminescence and/or a decrease in the rate of production of the emitting species in the multiphoton process. To distinguish between these two possibilities, we plotted the luminescence intensity vs. pressure in a similar manner to that in Fig. 5, but at different times after the maximum of the signal. A shift of the pressure transition to lower values between the two regimes is clearly observed. This shift can be explained in terms of a cumulative luminescence quenching process induced by collisions; furthermore, it would not

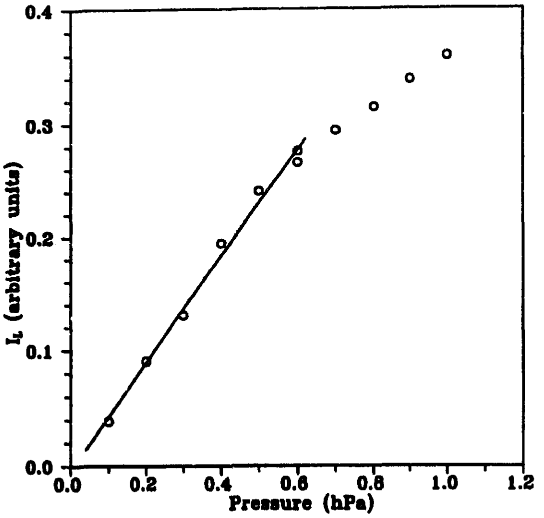

Fig. 5. CES pressure dependence of the peak luminescence intensity at 650 nm. $\phi = 75$ J cm^{-2}.

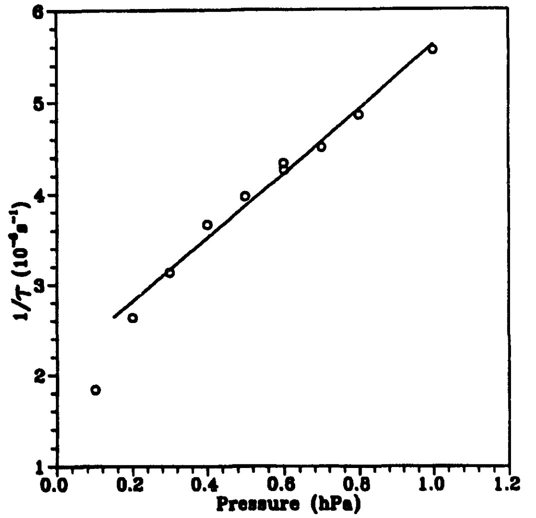

Fig. 6. Decay rate of the luminescence emission at 650 nm vs. the CES pressure.

take place if a change in the production rate of the emitting species was responsible for this shift.

Within the entire pressure interval studied here, the decay time profiles of the different signals can be fitted to a single exponential function, and the emission risetime (approximately 40 ns) does not change. From a plot of the decay rates as a function of the CES pressure (Fig. 6), we obtained a value of 480 ± 20 ns for the non-collisional radiative lifetime of the emitting species and a value of $(1.44 \pm 0.08) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for the quenching rate constant.

In Fig. 7, the intensity of the spontaneous luminescence at 650 nm vs. the fluence of the IR laser beam is presented for an initial pressure of 0.5 hPa. The threshold fluence for the occurrence of luminescence is about 12 J cm^{-2}, which is higher than the threshold for obtaining multiphoton dissociation (less than 0.4 J cm^{-2}) [6]. This indicates that the main source of emission is not the parent molecule, but an excited photoproduct [14]. In Fig. 7, we can also see that the decay

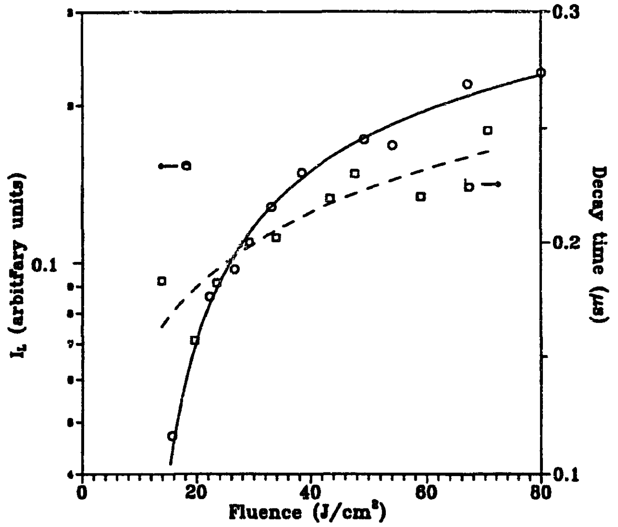

Fig. 7. Dependence on the CO_2 laser beam fluence of the luminescence peak intensity at 650 nm (○) (a) and the signal decay time (□) (b). $P = 0.5$ hPa.

time increases with the fluence, showing less quenching of the luminescence as this parameter is increased. We observed that, for all the experimental conditions studied, the onset of luminescence emission is delayed with respect to the onset of the laser pulse. The extent of this delay depends on the fluence of the laser beam: the lower the laser fluence, the longer the delay, exceeding in some cases the time to the laser pulse maximum. However, the delay time is independent of the substrate pressure. This delay has been ascribed to the finite time interval required to accumulate sufficient energy in a single molecule by the successive absorption of photons before dissociation occurs [15].

Visible or UV emissions, induced by collisionless infrared excitation and dissociation of polyatomic molecules, have been explained by the mechanism known as "inverse electronic relaxation" (IER) [16]. This mechanism is based on the coupling that occurs in some molecules between the excited vibrational ground state levels and those levels of the first excited electronic state lying in the same energy region. These mixed states are excited in the multiphoton process and can undergo subsequent de-excitation to the ground electronic state, thus giving rise to radiation emitted in the visible or UV region. The IER process can take place either in the parent molecule or in the newly formed fragment. Other explanations for the luminescence emission involve the recombination of radicals or subsequent chemical reactions between the fragments formed [9]. The lack of dependence of the delay between the laser pulse and the onset of luminescence on the substrate pressure rules out the last two explanations.

From this result and the threshold character of the fluence dependence of the luminescence, we suggest that the most probable reason for the production of visible emission in the IRMPD of CES is the IER of a primary fragment formed within the laser pulse.

Silylene absorption [17,18] has a long progression in the bending mode (ν_2) due to the large change which takes place in the bond angle on electronic excitation [18]. It has been verified [19] that the emission band originating from the bending vibrational transitions $(0, \nu'_2, 0) \rightarrow (0, \nu''_2, 0)$ should extend into the range 500–800 nm. These considerations allow the observed luminescence to be assigned to the decay from the $^1B_1$ electronic state to the $^1A_1$ ground state of silylene. Furthermore, the detected maximum at about 650 nm coincides with the $(0, 1, 0) \rightarrow (0, 1, 0)$ transition. This result may be expected if we consider that the corresponding Franck–Condon factor is the largest of those of the first seven $(0, \nu'_2, 0) \rightarrow (0, \nu''_2, 0)$ transitions [18]. In addition, the dissociation of the SiH_4 molecule at high fluence gives rise to a spontaneous luminescence with a similar spectrum which has been assigned to the same transition of silylene [19].

The lifetimes of emitting electronic states in IER processes are about 40–100 times longer than the lifetimes of spontaneous dipole-allowed transitions in a molecule [16]. On the other hand, a wide variation in the decay times between individual rovibronic levels of SiH_2 ($\tilde{A}^1B_1$), ranging from approximately 10 ns to more than 1 μs, has been reported [19–21]. The experimental value of 480 ns found for the radiative lifetime of the luminescence emission is in accordance with the lifetimes for transitions from the $^1B_1$ electronic state to the $^1A_1$ ground state of silylene induced through an IER process.

The occurrence of dissociation pathways different from Eq. (1) and Eq. (2) could give rise to the production of other open-shell species, such as HSiCl, Si, SiH or SiH_3. However, the maxima of their fundamental emission bands are not close to 650 nm. SiH emits a well-resolved structure in the range 405–420 nm [22], whereas the longest wavelength emission of SiH_3 and the main lines of Si are in the UV region [23,24]. HSiCl shows its main absorption progression extending from 410 to 480 nm [25].

The presence of SiH_2 agrees with the dissociation reaction pathways in the IRMPD of CES given in Eq. (1) and Eq. (2). Channel (1) was found to be the main process in the IRMPD of CES at fluences lower than 4 J cm^{-2} [6]. Under the experimental conditions used in this work, the nearly instantaneous formation of silylene suggests that the chloroethene elimination channel (Eq. (2)) is predominant. This is not unexpected if we consider the high fluence reached in the focused geometry, which allows a large amount of energy to be stored in the excited parent molecule, thus favouring the dissociation through the channel with the higher energy barrier.

4. Conclusions

Luminescence emitted in the IRMPD of CES has been detected under collision-free and collisional conditions. The radiative lifetime of this emission and the quenching rate by homogeneous collisions have been calculated. The luminescence has been assigned to the SiH_2 fragment formed, which is electronically excited through an IER process, and decays from the $^1B_1$ electronic state to the $^1A_1$ ground state. The detection of silylene supports the reaction pathways previously postulated for the IRMPD of CES and suggests that, at high fluence, the chloroethene elimination channel dominates the dissociation reaction. To confirm unequivocally the branching ratios for fragmentation following the IRMPD of CES, measurements of laser-induced fluorescence and IR fluorescence are in progress.

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References

[1] J.A. O'Neil, M. Horsburg, J. Tank, K.J. Grant, G.L. Paul, J. Am. Ceram. Soc. 72 (1989) 1130.
[2] J. Pola, Z. Bastl, J. Tláskal, H. Beckers, H. Bürger, P. Moritz, Organometallics 12 (1993) 171.
[3] J. Pola, Z. Papoušková, Z. Bastl, J. Tláskal, Appl. Phys. A 56 (1993) 313.
[4] J. Pola, Z. Bastl, J. Šubrt, R. Taylor, J. Mater. Chem. 5 (1995) 1345.
[5] J. Pola, Z. Bastl, J. Šubrt, J.R. Abeysinghe, R. Taylor, J. Mater. Chem. 6 (1996) 155.
[6] M. Santos, L. Díaz, Z. Bastl, V. Hulínský, M. Urbanová, J. Vítek, J. Pola, J. Mater. Chem. 6 (1996) 975.
[7] A.W.P. Jarvie, Organometal. Chem. Rev. A 6 (1970) 153.
[8] J. Pola, in: V. Chvalovsk, J.M. Bellama (Eds.), Carbon-Functional Organosilicon Compounds, Plenum, New York, 1984, p. 35.
[9] H. Reisler, C. Wittig, in: J. Jortner, R. Levine, R. Rice (Eds.), Photoselective Chemistry, Advances in Chemical Physics Series, vol. 46, Wiley, New York, 1981, pp. 679–711.
[10] R.V. Ambartzumian, N.V. Chekalin, V.S. Doljikov, V.S. Letokhov, E.A. Ryabov, Chem. Phys. Lett. 25 (1974) 515.
[11] C.M. Michael, Y. Lazarou, P. Papagiannakopoulos, Chem. Phys. Lett. 194 (1992) 415.
[12] S.A. Trushin, Y. Ishikawa, S. Arai, J. Chem. Soc., Faraday Trans. 91 (1995) 597.
[13] K.L. Kompa, H. Lamprecht, H. Schröder, A.A. Puretzky, V.V. Tyakht, J. Chem. Phys. 84 (1986) 2020.
[14] G. Hancock, D.E. Heard, J. Chem. Soc., Faraday Trans. 87 (1991) 1039.
[15] Y. Haas, in: J. Jortner, R. Levine, R. Rice (Eds.), Photoselective Chemistry, Advances in Chemical Physics Series, vol. 46, Wiley, New York, 1981, pp. 713–733.
[16] A.A. Puretzky, V.V. Tyakht, in: V.S. Letokhov (Ed.), Laser Spectroscopy of Highly Vibrationally Excited Molecules, Adam Hilger, New York, 1989, p. 329.
[17] I. Dubois, Can J. Phys. 46 (1968) 2485.
[18] M. Fukushima, S. Mayama, K. Obi, J. Chem. Phys. 96 (1992) 44.
[19] E. Borsella, L. Caneve, Appl. Phys. B 46 (1988) 347.
[20] J.W. Thoman Jr., J.I. Steinfeld, Chem. Phys. Lett. 124 (1986) 35.
[21] J.W. Thoman Jr., J.I. Steinfeld, R.I. Mckay, E.W. Knight, J. Chem. Phys. 86 (1987) 5909.
[22] R.W. Pearse, A.G. Gaydon, The Identification of Molecular Spectra, Chapman and Hall, London, 1965.
[23] G. Olbrich, Chem. Phys. 101 (1986) 381.
[24] A.A. Radzig, B.M. Smirnov, Reference Data on Atoms, Molecules and Ions, Springer Series in Chemistry and Physics, Springer, 1985.
[25] G. Herzberg, R.D. Verma, Can. J. Phys. 42 (1964) 395.