

ABOUT ROTATIONAL TEMPERATURE MEASUREMENTS AND THERMODYNAMIC EQUILIBRIUM IN RF GLOW DISCHARGES

Spyros STAMOU, Dimitris MATARAS and Dimitris RAPAKOULIAS

Laboratory of Plasma Chemistry

Department of Chemical Engineering, University of Patras

P.O.Box 1407, 26500, Patras, Greece

e-mail: dim@chemeng.upatras.gr

ABSTRACT. The rotational temperature of the $A^2\Delta$ excited state of SiH has been determined in a silane r.f. glow-discharge by optical emission spectroscopy, using both a revised Boltzman diagram method and a detailed simulation of the emission spectrum utilising a least squares fitting (LSF) method. It is shown here that the LSF is more reliable and a careful use can lead to accurate results. This is accomplished by using an improved term value formula and an optimisation of the set of constants are used to calculate the best possible simulation of the spectrum. On the other hand, important informations about the achievement of thermodynamic equilibrium are obtained, with the use of the Boltzman plot method. It is shown that the population distribution in the rotational levels of a short-lived electronic state is well described by Boltzman statistics. In both methods, the experimentally determined FWHM of the optical system is of major importance.

KEYWORDS: *Rotational temperature, emission spectroscopy, silane, simulation, Boltzman*

1. INTRODUCTION

Many different techniques have been used to measure rotational and vibrational temperatures of excited molecular fragments in gas discharges. These include microwave absorption, infrared absorption, optical emission and laser-induced fluorescence [1]. The most commonly used technique is the analysis of the intensity distribution in the rotational fine structure of electronic transitions. The measurement of these temperatures

can give access to information about the electron impact excitation or dissociative excitation processes as a function of the various correlated plasma parameters and/or their evolution as a function of the discharge space [2].

Among the methods employed for the determination of the rotational temperature T_{ROT} the most widely used is, without doubt, that of the Boltzman plot. However, this is not applicable in cases where rotational structure cannot easily be resolved. For example, this situation occurs in the case of the emission spectrum of SiH where Λ -doubling occurring in the $^2\Pi$ ground state, in combination with partial overlapping of the branches forms an intricate structure which cannot be resolved with the experimentally determined FWHM of the optical system being 0.144 Å. Generally, in such cases a simulation of the emission spectrum is attempted assuming that Boltzman statistics hold well and using T_{ROT} as a parameter [3]. This approach was adopted in the past by this group to obtain an improved simulation of the $A^2\Delta \rightarrow X^2\Pi$ transition of SiH [4]. In this work, it is shown that a Boltzman plot can be created employing a deconvolution procedure of the Λ -doublets, utilizing the known instrument function. The rotational temperature values obtained in this way exhibit large standard deviation compared to the simulation method. In fact, the main advantage of this modified Boltzman plot is the ability to check the validity of the assumption of Boltzman statistics in non-equilibrium plasma diagnostics.

2. EXPERIMENTAL

The experimental setup is described in detail elsewhere [5]. Briefly, the chamber is a 160 mm wide cylinder, made of stainless steel, equipped with four quartz windows suitable for optical measurements. The cell is equipped with cylindrical electrodes, 55 mm in diameter. Pressure is measured by a capacitance manometer and can be adjusted independently from the flow rate, within the region of interest, by using mass flow controllers and downstream pressure control by a throttling valve. Matheson ultra-high purity silane was used in all cases, while the system was baked out and pumped down to 10^{-7} Torr prior to the experiments. The power consumed by the discharge is measured with the technique proposed in ref. 3. All the measurements are performed in low-power and low-pressure conditions. The formation of powder, by homogeneous nucleation in

the gas phase is controlled by using a laser scattering technique [4]. Thus, all the measurements presented here are performed in particle free conditions.

The emission from a pure silane discharge is collected by a collimating lens and then focused with a second lens at the entrance slit of a Jobin Yvon THR-1000 1 m focal length monochromator. The apparatus is equipped with a plane ruled grating of 3600 grooves per millimetre. The widths of the entrance and exit slits were 150 μm and 160 μm respectively, for the specific experiments. The light intensity at the exit slit is recorded using a Hamamatsu 1P28 side-on photomultiplier tube (PMT) with an optimum signal to noise ratio for a cathode voltage of -800 Volts. The scan speed of the monochromator was 1 $\text{\AA}/\text{min}$. The FWHM of the instrument, which is a critical parameter as will be discussed later, is determined using the 4158 $\text{\AA}$ emission line from an Ar discharge. The shape of the instrument line profile is either triangular or trapezoidal, for equal or unequal slit widths respectively. However, the difference between the two cases on the peak height is practically negligible, permitting the use of a triangular distribution. The experimentally measured FWHM for these slit widths is 0.144 $\text{\AA}$.

3. THEORY

The production of SiH^* in silane r.f. discharges is through the formation of dissociative Rydberg states of SiH_4 by electron impact. More specifically, the vacuum ultra violet (VUV) study of SiH_4 has revealed the Rydberg nature of the observed absorption bands [6,7]. The subsequent dissociation generally leads to highly excited fragments due to the excess of energy contained in the Rydberg states, the excitation being electronic, vibrational, rotational but mostly translational. It is known, that most of the excess energy is imparted to fragments as kinetic energy and the heaviest SiH_n atoms are expected to separate with a much smaller velocity than hydrogen atoms [8]. The dissociative excitation of SiH_4 studied in the past [9], has revealed an appearance potential of 10.5 ± 0.5 eV for the $A^2\Delta$ excited state of SiH while intense rovibrational excitation was detected in the transition to the ground state [3]. More specifically, once a radical is formed, it can spontaneously radiate to a lower level, it can be collisionally quenched to a different vibronic level or it can suffer a collision that causes a change of

the population distribution in the rotational levels within the same electronic vibrational level. This population re-distribution on the excited rotational levels is possible if rotation-changing collisions occur during the lifetime of the excited level. Although glow-discharges operate in non-equilibrium conditions, there are degrees of freedom that the population distribution can be well described by Boltzman statistics. More specifically, the relative population of rotational levels in a long-lived electronic vibrational level of a diatomic molecule can be described by a Boltzman distribution with a rotational temperature T_{ROT} . The rotational distribution in a short-lived electronic vibrational state may be or may not be equilibrated depending on the relative size of rotational redistribution rates versus total quenching rates.

The theoretical description of the rotational energy levels of diatomic molecules in $^2\Pi$ electronic states, such as SiH, is well known from the work of Hill and Van Vleck [10]. The $^2\Pi$ diatomic molecules exhibit two characteristics that must be considered since they influence the distribution of the rotational energy levels.

The first is Λ -doubling which removes the degeneracy associated with levels of the same $|\Omega|$ and J . The phenomenon of Λ -doubling generally is considered in chemical dynamics as a negligible spectroscopic effect. More specifically, the corresponding energetic splittings are normally negligible compared to other internal energies or to collision energies. However, preferential population of one member of a Λ -doublet pair has been observed in chemical reactions, inelastic collisions, photodissociation and surface scattering [11]. In the conventional theory of Λ -doubling in $^2\Pi$ states, the Λ -type splitting may be expressed to second order in terms of the parameters p and q using the Mulliken and Christy formula [12]. Deviations from this formula observed for $J > 13.5$ can be predicted in some cases incorporating corrections due to centrifugal distortion [13]. However, in the case of SiH such corrections cannot describe the observed splittings. Λ -doubling is likely to occur in the $A^2\Delta$ excited state also, although it is considered to be negligible.

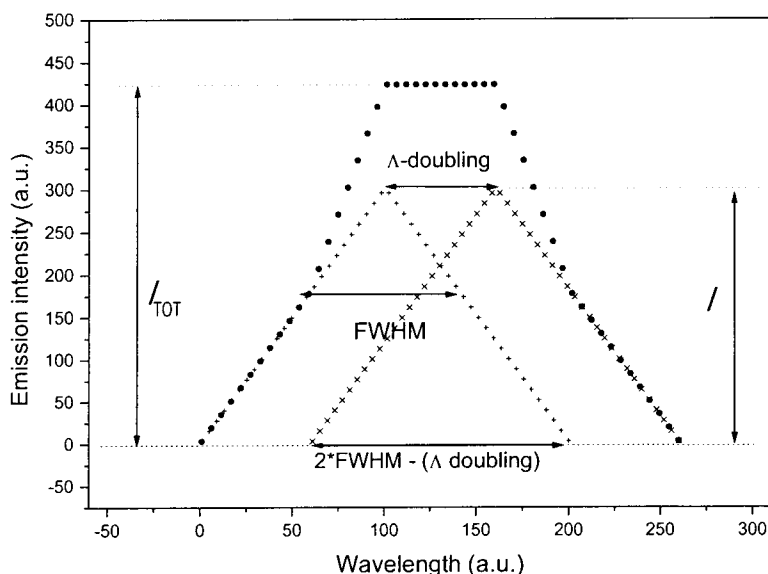
The other effect is the rotational distortion of the spin multiplets and corresponds to the increase in the separation of $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ components with increasing rotation of the nuclei. Physically, this is due to the gradual transition of a molecule from Hund's case (a), where the spin is strongly coupled to the molecular axis and Σ is a good

quantum number, to Hund's case (b), where Coriolis forces have uncoupled spin from the molecular axis and Σ is no longer a good quantum number. Therefore, rigorous expressions for the rotational term values of a diatomic molecule which take into account the effect of centrifugal distortion on the spin multiplets are required.

4. METHODS FOR THE DETERMINATION OF THE ROTATIONAL TEMPERATURE

4.1. The Boltzman plot method

The determination of the rotational temperature of an excited state through the emission spectrum, is a routine procedure most of the time. The Boltzman plot method, which is widely used for this purpose, exhibits many advantages such as, simplicity in use and very good sensitivity. At the same time, informations concerning the achievement of thermodynamic equilibrium are obtained, which are very important especially in low-pressure plasmas. The use of the Boltzman plot, however, requires a spectroscopic system with an adequate resolution to split adjacent emission lines. In the case of SiH, it is not possible to fulfil this requirement with moderate spectrometers, due



to Λ -doubling in the ground state, as mentioned earlier. For this, rotational temperature measurements of SiH performed in the past [3,14], were based on the simulation of the emission spectrum. The simulation method will be later discussed in details.

A new approach on the application of the Boltzman plot method in an unresolved spectrum, due to Λ -doubling, is presented here. The novelty consists in the application of a deconvolution procedure on the experimental peak heights, utilising the known FWHM value of the optical system. It must be noted that the experimentally determined FWHM value used in this work is a key parameter in this approach. Thus, figure 1 presents the calculation of the original height of the Λ -doublet component, assuming equal sharing of the population of the upper rotational level to the ground state doublets. More specifically, the intensity I of the individual Λ -component can be expressed in terms of the known parameters FWHM and Λ -doubling as follows:

$$I = \frac{FWHM * I_{TOT}}{2 * FWHM - \Lambda doubling} \quad (1)$$

Furthermore, it is known that the intensities of the emission lines I_{em} can be expressed in terms of line strengths S_J ⁵, as follows:

$$I_{em} = \frac{Cv^4}{Q_{ROT}} S_{J'} \exp(-E(J')hc/kT_{ROT}) \quad (2)$$

where C is a constant, v is the transition wavenumber, T_{ROT} is the rotational temperature, $E(J')$ is the energy level of the upper electronic state having the J' rotational level and Q_{ROT} is the rotational partition function in the case of SiH being:

$$Q_{ROT} = \frac{2kT_{rot}}{hcB_v} \quad (3)$$

where B_v is the rotational constant associated to the v' vibrational level. With the use of the calculated peak heights from equation 1, one can plot the function of I as follows from equation 2, as a function of $E(J')$ and calculate the rotational temperature from the slope of the resulting line.

4.2. The simulation method

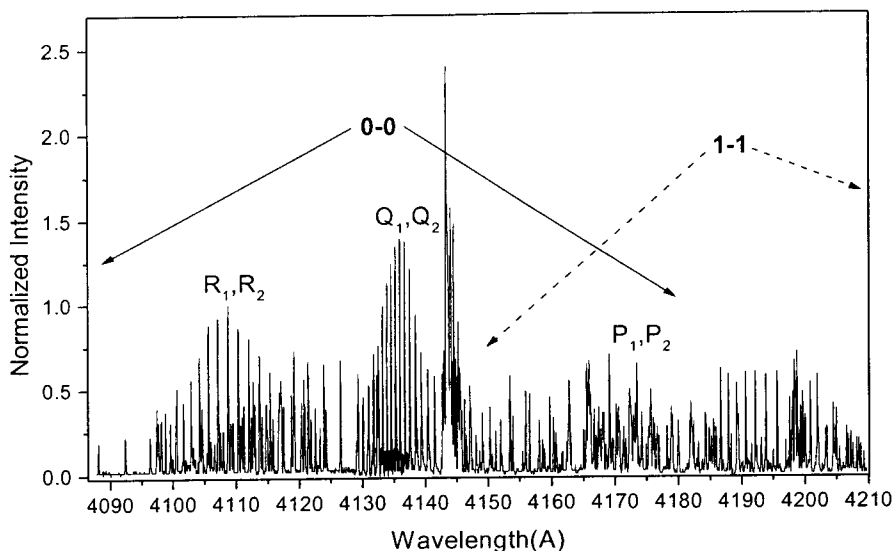
Besides the Boltzman plot method, the measurement of rotational temperature can

be performed based on the minimisation between the experimental emission spectrum and the corresponding simulation spectrum. The complete procedure to simulate the emission spectrum mentioned above is described in ref. 4, so only a brief description will be given here. First, one has to calculate the rotational energy levels of the states involved in the transition using the appropriate term value formulas. For a doublet transition which is our case, recently, Balasubramanian et al [15] rederived an improved term value formula, which results in a better simulation of the experimental spectrum, compared to other formulas, found in literature [4]. The transition wavelengths are calculated by subtracting the energies of the rotational levels of the upper and lower states calculated from the previous step according to the appropriate selection rules. Finally, one has to calculate the theoretical spectrum using an instrument function usually of triangular form to convolute the calculated intensities. The convolution procedure is critical in the case of closely spaced lines, such as Λ -doublets, because it is exactly the resulting peaks that are used for the determination of the rotational temperature. This fact enhances also the importance of the FWHM value, as mentioned above.

In order to calculate the rotational temperature value T_{ROT} of a given experimental spectrum one has to compare the simulated spectrum with the experimental one, using T_{ROT} as parameter. For this, different criteria have been used in the past, such as the minimal surface criterion (MSC) or the homothetic parallelism criterion (HPC) as referred in ref. 16. A least squares fitting (LSF) method is used here as described by the following error function:

$$\epsilon = \sum_{i=1}^N \left(\frac{I_{i,\text{exp}}}{I_{\text{exp}}^{\text{max}}} - \frac{I_{i,\text{sim}}}{I_{\text{sim}}^{\text{max}}} \right)^2 \quad (4)$$

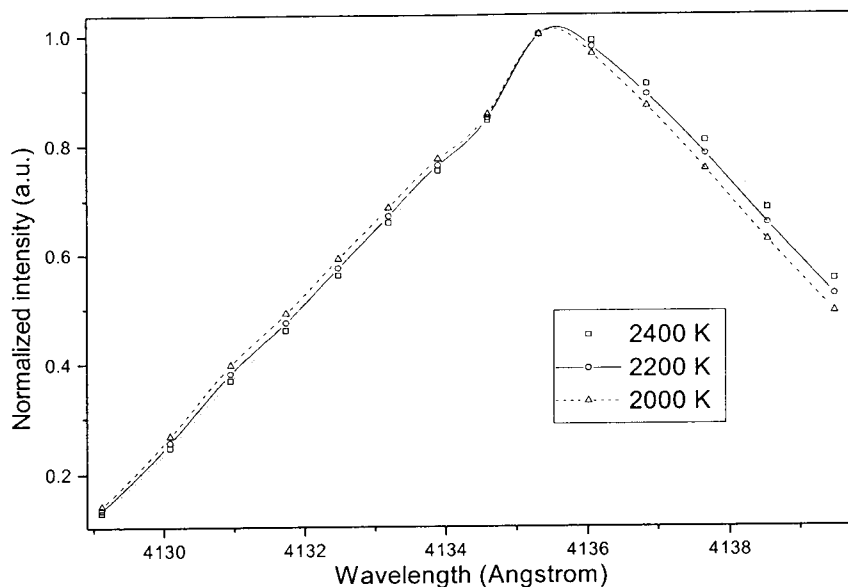
where the suffixes “exp” and “sim” stand for experimental and simulated intensities respectively, while “max” stands for maximum intensity and N is the number of peaks. The minimisation of the error function can be used as a criterion revealing, not only the effectiveness of the simulation method in general, but also the influence of various “parameters”, such as the values of the molecular constants or formulas, on the calculation of the rotational temperature. This approach has been recently used by this group, to develop an improved simulation of the $A^2\Delta-X^2\Pi$ transition of SiH [4].



5. RESULTS AND DISCUSSION

Figure 2 presents a typical emission spectrum recorded from a 75 mTorr, 2 mW/cm², radio-frequency (r.f.) pure silane discharge. The characteristic $A^2\Delta-X^2\Pi$ transition of SiH shown in figure 1 is a doublet between a Δ upper state in Hund case (b) ($Y \approx 0.48$) and a Π ground state intermediate between cases (a) and (b) ($Y \approx 19.3$), depending on the J value. A partial overlapping of the 0-0 and the 1-1 bands in the region of P_1 , P_2 branches of the 0-0 band is shown, whereas the H_δ line (4101.7 Å), possibly observed in silane discharges, is not present. Furthermore, Λ -type doubling occurs in the ground state, so each observed peak is composed of two closely placed lines.

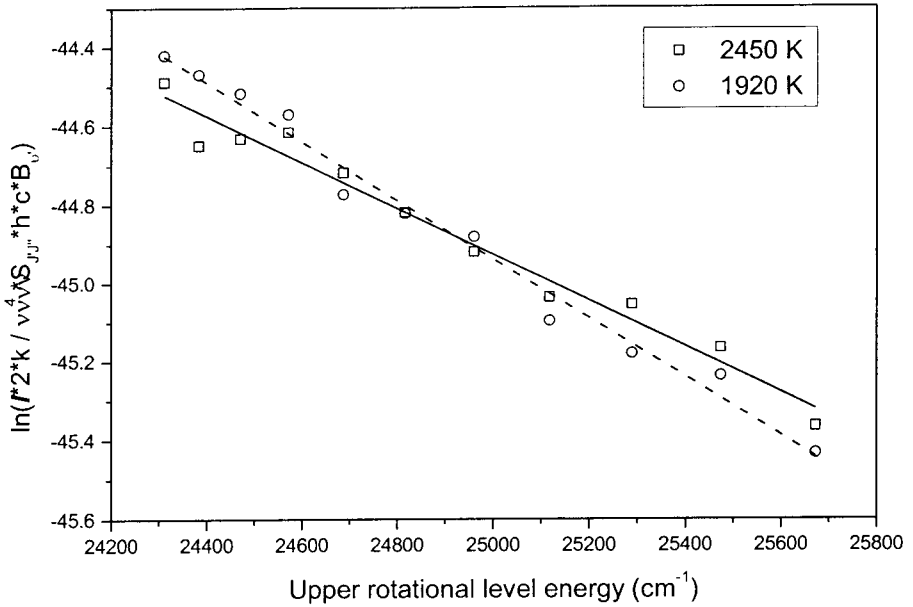
Figure 3 presents the calculated Q_1 branch profile, varying T_{ROT} in the 2000-2400 K range. The intensities presented here are normalised to the maximum peak height each time, exhibiting thus the relative changes of the peak heights. It is obvious that the tail of the branch, i.e. beyond 4136 Å, corresponding to large values of the angular momentum J , is more sensitive in changes of the rotational temperature compared to the beginning of the branch. This means that the more accurate are the calculations for large quantum numbers J , the more accurate is the measurement [4]. In addition, it is clear that



the method exhibits very good sensitivity since even small changes in the peak heights will result in a different T_{ROT} .

The two methods described above are utilised to perform rotational temperature measurements at two different experimental conditions. Namely, two emission spectra were recorded, both at 75 mTorr, using 75 V and 150 V r.f. peak to peak voltage, resulting in 2 mW/cm^2 and 8 mW/cm^2 power consumption respectively.

Figure 4 presents the Boltzman plot created using the procedure described above. It is clearly shown that the population distribution follows a Boltzman law. In principle, this is not expected since this is a short lived electronic state, having a lifetime of about 500 ns [17]. It appears, though, that there is a complex interplay of elementary collisional processes in non-equilibrium plasma. The rotational temperature values calculated are 2450 K and 1920 K for the high and low power consumption respectively. However, the calculated slope value, and thus T_{ROT} , exhibits a very sensitive dependence on the measured peak heights. This means that possible errors, due to electrical noise superimposed on the signal for example, during the recording of the spectrum, induce a significant decrease in the measurement accuracy. In fact, temperature differences of



200 K were encountered in some cases. This inaccuracy is an inherent characteristic of the method and is due to the sensitivity of the calculated slope value, on the experimental measurements. Nevertheless, the Boltzman plot is rather useful because it can provide information about the achievement of thermodynamic equilibrium, which is often a matter of dispute in low-pressure plasmas. Furthermore, the fitting of data presented on figure 4 confirms the fact that the Boltzmann exponential used in equation (2) describes very well the population distribution of the rotational levels.

The respective rotational measurements using the simulation method are presented in figures 5a and 5b. In both cases, a very good simulation of the experimental peak heights, presented with hollow square symbols on the figures, is obtained. In fact, the values of T_{ROT} obtained with this method are more objective compared to the Boltzman plot values. This is also confirmed by the smaller standard deviation of 50 K encountered in this case. The apparent advantage is related with use of the least squares fitting method as described in equation 4. More specifically, it is found that the comparison of simulated and experimental spectra towards the minimum ϵ value, is not influenced so much by the uncertainty of the measurement of the experimental peak heights. On the other hand, the

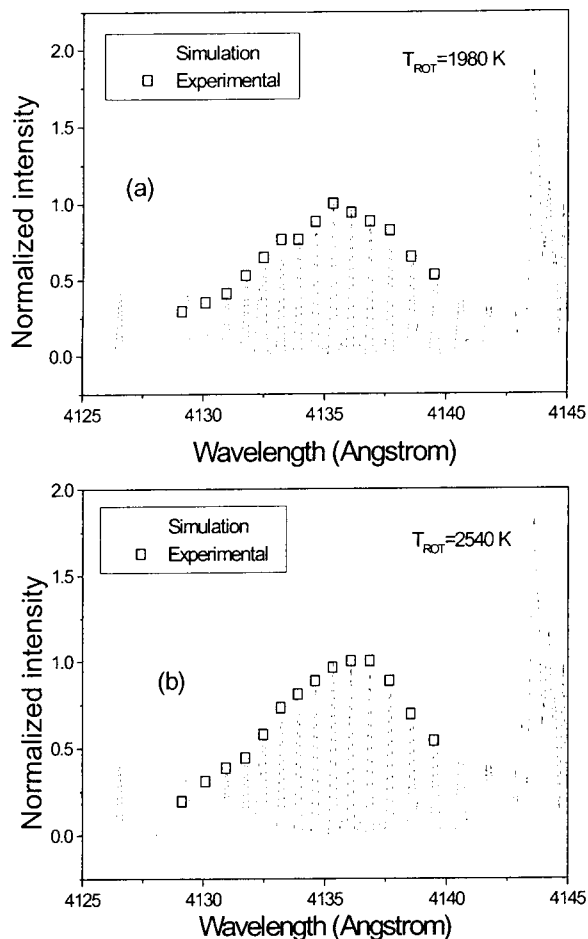


Figure 5. Simulation of the experimental peak heights indicated as open squares for a 75 mTorr, (a) 2 mW/cm² and (b) 8 mW/cm² pure silane discharge

sensitivity of the method is still quite good as discussed earlier.

5. CONCLUSIONS

The rotational temperature of SiH in silane r.f. glow-discharge has been determined by optical emission spectroscopy, using two different techniques. In both techniques, the FWHM of the optical system was experimentally determined. First, a Boltzman plot was created based on a novel approach, consisting in a deconvolution procedure of the experimental peak heights. Second, a simulation of the 0-0 band of the $A^2\Delta-X^2\Pi$ transition of SiH is utilized towards a more objective

determination of T_{ROT} . The results of the two methods are totally compatible, however, the L.S.F. method can lead to safer and more accurate conclusions if used carefully. On the other hand, the Boltzman plot method presented here can be used to extract important information concerning the achievement of thermodynamic equilibrium. Thus, it was found that the population distribution in a short lived electronic state, such as $A^2\Delta$, is

well described by Boltzman statistics. In this way, the use of the revised Boltzman plot presented here is proven valuable since the validity of the assumption of the Boltzman law in the various modeling studies of low-pressure plasmas can be well controlled.

REFERENCES

- [1] I. Ishii and A. Montaser, Spectr. Acta **46B**, (1991) 1197
- [2] G. Turban, B. Drevillon, D. Mataras and D. E. Rapakoulias in *Plasma deposition of amorphous silicon based materials* edited by G.Bruno, P.Capezzuto and A.Madan (Academic Press, London, 1995) p.63
- [3] J. Perrin and E. Delafosse, J. Phys. D: Appl. Phys., **13**, (1980) 759
- [4] S. Stamou, D. Mataras and D. Rapakoulias, Chem. Phys. **218**, (1997) 57
- [5] D. Mataras, S. Cavadias and D. Rapakoulias, J. Appl. Phys. **66**, (1989) 119
- [6] M. Suto and L.C. Lee, J. Chem. Phys. **84** (1986) 1160
- [7] C. Larrieu, D. Liotard, M. Chaillet and A. Dargelos, J. Chem. Phys. **88** (1987) 3848
- [8] J. Perrin and J.P.M. Schmitt, Chem. Phys. Lett. **112** (1984) 69
- [9] J. Perrin and J.F.M. Aarts, Chem. Phys. **80** (1983) 351
- [10] E. Hill and J. H. Van Vleck, Physical Review, **32**, (1928) 250
- [11] P. Andresen and E. W. Rothe, J. Chem. Phys., **82**, (1985) 3634
- [12] R. S. Mulliken and A. Christy, Physical Review, **38**, (1931) 87
- [13] L. Veseth, J. Phys. B.:Atom, Molec. Phys., **3**, (1970) 1677
- [14] S. Tsurubuchi, K. Motohashi, S. Matsuoka and T. Arikawa, Chem. Phys. **161** (1992) 493
- [15] T. K. Balasubramanian, A. S. P. Rao, R. D'Souza and N. A. Narasimham, Act. Phys. Hung. **55** (1984) 27
- [16] A. Chelouah, E. Marode, G. Hartmann and s. Achat, J. Phys. D.: Appl. Phys., **27**, (1994) 940
- [17] M. Nemoto, A. Suzuki, H. Nakamura, K. Shibuya and K. Obi, Chwm. Phys. Lett. **162** (1989) 467