

Absolute primary H atom quantum yield measurements in the 193.3 and 121.6 nm photodissociation of acetylene

A. Lauter ^a, K.S. Lee ^b, K.H. Jung ^b, R.K. Vatsa ^c, J.P. Mittal ^c, H.-R. Volpp ^{a,*}

^a *Physikalisch-Chemisches Institut, Universitat Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, Germany*

^b *Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Taeduck Science Town, Taejon 305-701, Republic of Korea*

^c *Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*

Received 5 March 2002; in final form 5 March 2002

Abstract

Absolute quantum yields for primary H atom formation (Φ_{H}) were measured under collision-free conditions for the room-temperature gas-phase dissociation of acetylene (C_2H_2) after photoexcitation at 193.3 nm and at the H-atom Lyman- α wavelength (121.6 nm) by a pulsed laser photolysis (LP)–laser-induced fluorescence (LIF) ‘pump-and-probe’ technique. Using HCl and CH_4 photolysis at 193.3 and 121.6 nm, respectively, as a reference, values of Φ_{H} (193.3 nm) = 0.94 ± 0.12 and Φ_{H} (121.6 nm) = 1.04 ± 0.16 were obtained which demonstrate that for both photolysis wavelengths the H + C_2H product channel dominates the primary C_2H_2 photochemistry. © 2002 Published by Elsevier Science B.V.

1. Introduction

Acetylene (C_2H_2) plays an important role in combustion chemistry [1]. In addition, its primary ultraviolet (UV) and vacuum-ultraviolet (VUV) photolysis as well as the subsequent chemistry of the resulting photoproducts such as ethynyl radicals (C_2H), which can catalyze the decomposition of methane [2], play a crucial role in the atmospheric chemistry of the outer planets and their moons (see e.g. [3] and references therein). As a consequence, a number of experiments were per-

formed in order to determine primary quantum yields for product formation at various photolysis wavelengths (193.3 nm [4–6], 184.9 nm [7], 147.0 nm [8], and 123.6 nm [9]). The results of these studies, which were mainly performed employing static sample photolysis along with stable end-product analysis [6–9], indicated that the quantum yield for the simple C–H bond fission channel H + C_2H is only 0.1–0.3 (see [6, Table 1]) and it was proposed that the major primary photochemical process is the formation of an electronically excited metastable acetylene ($\text{C}_2\text{H}_2^{**}$) [6,10] and/or vinylidene (H_2CC^{**}) [11]. In addition, a large number of state-resolved dynamics studies were performed to investigate the photofragmentation process of the H + C_2H product channel in

* Corresponding author. Fax: +49-(0)6221-545-050.

E-mail address: aw2@ix.urz.uni-heidelberg.de (H.-R. Volpp).

the ground-state (see e.g. [12–15] and references therein) as well as in the vibrationally mediated [16,17] UV photodissociation of C_2H_2 under collision-free conditions. These studies along with VUV photodissociation dynamics experiments in the wavelength range 121.2–132.2 nm [18] and at the Lyman- α wavelength (121.6 nm) [18–20] allowed to gain detailed insight into the primary fragmentation dynamics of the $H + C_2H$ product channel. However, as outlined in [14,15], these dynamics studies, in particular $H + C_2H$ predissociation reaction time measurements in the photolysis wavelength range 206–216 nm [15], in which no indication for the formation of any metastable acetylene and/or vinylidene could be found, raised serious doubts concerning the validity of the low values of the $H + C_2H$ product channel quantum yields reported in the literature so far [4–9].

The focus of the work to be presented in this Letter was on the measurement of the absolute H atom quantum yield in the 193.3 nm and the Lyman- α (121.6 nm) photolysis of C_2H_2 under collision-free conditions. The experiments were performed in a low-pressure flow reactor at room temperature using the pulsed laser photolysis–vacuum-ultraviolet laser-induced fluorescence (LP–VUV–LIF) ‘pump-and-probe’ technique in combination with a photolytic calibration approach. In case of the 193.3 nm photolysis wavelength the present work can be regarded as a remeasurement, the result of which can be compared with the results of previous experiments [4–6]. For the atmospherically important Lyman- α wavelength (121.6 nm), on the other hand, there has been – to the best of our knowledge – no absolute value of the absolute H atom quantum yield reported so far.

2. Experimental

The experiments were carried out in a flow reactor at mTorr level pressures using a setup similar to the one previously used to study the 193.3 nm and Lyman- α photolysis of isocyanic acid (HNCO) [21,22]. Hence, only a summary of the experimental approach relevant to the present studies will be given.

C_2H_2 (Messer Griesheim, > 99.6%) was pumped through the reaction cell at room temperature. In order to ensure that possible acetone impurities are removed, the gas flow was passed through a cooling trap kept at $-80^\circ C$ before entering the cell. In the 193.3 nm and Lyman- α photolysis studies the C_2H_2 cell pressure was typically 7–10 mTorr. For the photolytic calibration measurements at 193.3 nm, HCl (Messer Griesheim, 99.99%) and for the calibration measurements at the Lyman- α wavelength, CH_4 (Messer Griesheim, 99.8%) was pumped through the cell at pressures of typically 16–25 and 35–40 mTorr, respectively.

In the first part of the present study the unpolarized output of an ArF excimer laser (193.3 nm emission wavelength, pulse duration 15–20 ns) was used as a ‘pump’ laser to dissociate the C_2H_2 parent molecules. As in [5], low pump laser intensities in the range 2–45 mJ/cm² were employed in order to avoid the photolysis of C_2H radicals. The latter process could lead to the formation of C_2 along with ‘secondary’ H atoms [23], which will, however, exhibit a quadratic dependence on the pump laser intensity. As depicted in Fig. 1a, in the present work a linear dependence of the H atom signal on the 193.3 nm pump laser intensity was observed within the experimental error indicating that C_2H photolysis can be neglected. In previous studies a linear dependence of the H atom signal on the pump laser intensity could be observed up to values of 100 mJ/cm² (see [4, Fig. 1]).

Pulsed narrow-band VUV-probe laser radiation (band width $\Delta\omega_{\text{probe}} \approx 0.35 \text{ cm}^{-1}$) – tunable around the H atom Lyman- α transition – was generated using the Wallenstein method [24] for resonant third-order sum–difference frequency conversion of pulsed dye laser radiation in a phase-matched Kr/Ar mixture in order to detect the nascent H atom photoproducts via ($2p^2 \text{ P} \leftarrow 1s^2 \text{ S}$) LIF [21,22]. As described in [25], maximum VUV pulse energies up to 20 μJ can be achieved with this method. In the present studies, however, the actual pulse energy was considerably lower due to absorption in the cell windows and optics. In all experiments the actual probe laser intensity was reduced until the desired intensity dependence of the H atom signal was obtained. The probe laser

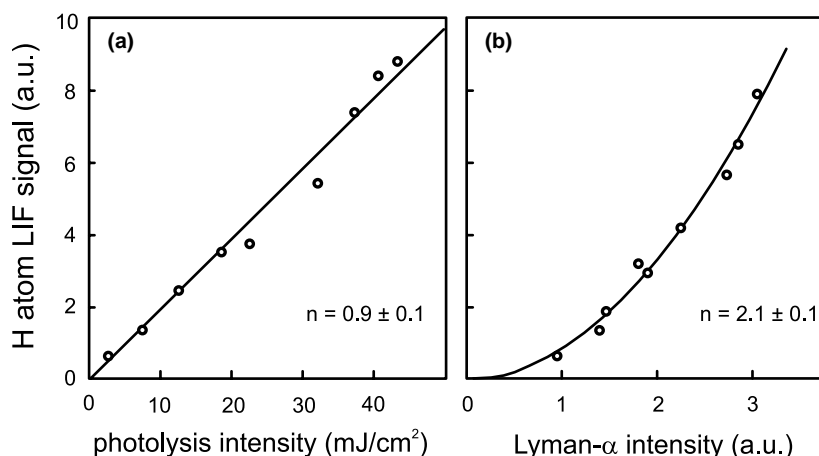


Fig. 1. Dependence of the H atom signal: (a) on the pump laser intensity in the 193.3 nm photolysis of C_2H_2 and (b) on the VUV pump–probe laser intensity as obtained in the C_2H_2 Lyman- α (121.6 nm) photodissociation experiments. Solid lines are the results of a fit to the experimental data to determine the power dependence n of the H atom LIF signal (the obtained values for n are given in the figure).

beam was aligned to overlap the pump laser beam at right angles in the viewing region of the LIF detector. The delay time between pump and probe laser pulses was typically 100 ± 5 ns, which allowed the collision-free detection of the nascent H atom products under the low-pressure conditions of the experiments. To avoid that the H atom quantum yield measurements are affected by ‘fly-out’ of H atoms from the detection region, the spatial overlap and the delay-time dependence of the H atom signal was carefully checked as described in [26]. In the two-color (193.3 nm pump and Lyman- α probe) photolysis experiments the ‘Lyman- α -self-photolysis-background’ subtraction method used in our previous HNCO UV photolysis studies was adapted to obtain a LIF signal which originates from H atoms solely produced by the 193.3 nm pump laser (see [21]).

In the second part of the present study, the Lyman- α VUV laser radiation was used to photodissociate the C_2H_2 parent molecules as well as to detect the nascent H atom photodissociation products within the same laser pulse under collision-free conditions (the duration of the laser pulse was about 10–15 ns). In all experiments special care was taken to separate the Lyman- α VUV laser radiation from the unconverted fundamental laser beams (see [21, Fig. 2]). The H atom LIF signal

was measured by a solar blind photomultiplier. During the experiments the VUV laser beam intensity was monitored with an additional solar blind photomultiplier. Each point of a recorded H atom Doppler profile as shown in Fig. 2 was averaged over 30 laser shots. All measurements were performed at a laser repetition rate of 6 Hz. The H atom LIF signal, UV pump, and VUV probe beam intensities were recorded with a boxcar integrator system.

In the two-color (193.3 nm pump and Lyman- α probe) experiments, care was taken that the observed H atom LIF signals measured in the C_2H_2 (see Fig. 1a) and in the HCl photolysis showed a

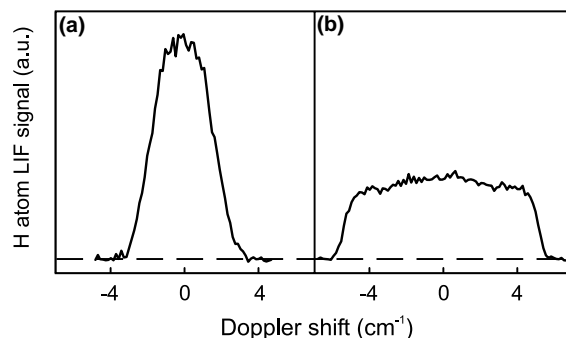


Fig. 2. H atom Doppler profiles measured in the 193.3 nm photolysis of: (a) 9 mTorr of C_2H_2 and (b) 17 mTorr of HCl.

linear dependence on the 193.3 nm pump laser and on the VUV probe laser intensities. In these experiments the H atom LIF signal was normalized point-by-point to the UV pump and Lyman- α VUV probe laser intensity.

In the one-color (VUV pump–probe) experiments the H atom LIF signal was normalized point-by-point to the square of the Lyman- α VUV (pump–probe) laser intensity. The ($n = 1 + 1$)-photon nature (one-photon dissociation of the parent C_2H_2 molecules followed by a one-photon H atom LIF-detection step) of the process was verified in experiments in which the VUV laser intensity was varied (see Fig. 1b). Similar measurements were performed in case of CH_4 where under comparable experimental conditions a value of $n = 2.0 \pm 0.1$ could be obtained. From the observed quadratic VUV intensity dependence one can conclude that secondary photolysis of photodissociation products can be neglected in the analysis and interpretation of the present results.

3. Results and discussion

3.1. H atom quantum yield in the 193.3 nm photolysis of C_2H_2

For the measurement of the absolute H atom quantum yield for C_2H_2 , the photolytic calibration approach described in [4,22,26] was employed in which the unknown H atom quantum yield in the 193.3 nm photolysis of C_2H_2 can be obtained by calibrating the respective H atom signal $S_H(C_2H_2)$ against the H atom signal $S_H(HCl)$ from well-defined H atom number densities generated by photolyzing HCl, for which the H atom quantum yield is unity. S_H stands for the integrated areas under the respective H atom Doppler profiles shown in Fig. 2. In the present work, the H atom quantum yield for C_2H_2 was determined employing the following expression [26]:

$$\Phi_H(193.3 \text{ nm}) = \gamma \left\{ \frac{S_H(C_2H_2) \sigma_{HCl} p_{HCl}}{S_H(HCl) \sigma_{C_2H_2} p_{C_2H_2}} \right\}, \quad (1)$$

where σ_{HCl} and $\sigma_{C_2H_2}$ are the optical absorption cross-sections of HCl, $(8.1 \pm 0.4) \times 10^{-20} \text{ cm}^2$ [27], and C_2H_2 , $(1.40 \pm 0.05) \times 10^{-19} \text{ cm}^2$ [6], respec-

tively, measured at the ArF excimer laser emission wavelength (193.3 nm). p_{HCl} and $p_{C_2H_2}$ are the pressures of HCl and C_2H_2 as employed in the measurement. In Eq. (1), the factor γ represents a correction, which accounts for the different degree of absorption of the Lyman- α radiation by HCl and C_2H_2 . In 84 independent calibration measurements, integrated areas under the H atom Doppler profiles were determined for the HCl and C_2H_2 photolysis which, using Eq. (1) yielded the following average value for the H atom yield in the 193.3 nm photolysis of C_2H_2 : $\Phi_H(193.3 \text{ nm}) = 0.94 \pm 0.12$. The experimental error was determined from the 1σ statistical uncertainty of the experimental data and the uncertainties of the optical absorption cross-sections using error propagation.

The $\Phi_H(193.3 \text{ nm})$ value obtained in the present work is considerably higher than the values obtained in the previous studies for the same photolysis wavelength [4–6]. A H atom quantum yield close to unity, as determined in the present work, indicates that the majority of the photoexcited C_2H_2 molecules undergoes dissociation to yield H atom and C_2H photoproducts. It can therefore be concluded that the formation of ‘nonreactive’ metastable acetylene and/or vinylidene in the 193.3 nm photolysis of C_2H_2 is of considerably less importance than previously thought [10,11]. This conclusion is in line with the results of previous experiments in the photolysis wavelength range 206–216 nm, in which no indication for the formation of any metastable acetylene and/or vinylidene could be found [15].

The present result further shows that in the C_2H_2 photolysis at 193.3 nm (which corresponds to an excitation energy of $51\,733 \text{ cm}^{-1}$) the quantum yield of the only other thermodynamically allowed photodissociation channel, $H_2 + C_2(X^1\Sigma_g^+)$ ($D_0 \approx 50\,000 \text{ cm}^{-1}$ [28]), must also be only of minor importance. This result is in agreement with previous studies, in which no C_2 radicals could be detected for photolysis laser intensities below 25 mJ/cm^2 [23]. As demonstrated, e.g., in [13,29], at higher photolysis laser intensities C_2 radicals can be formed via secondary photolysis of C_2H radicals in combination with ‘secondary’ H atoms which are faster than the ‘primary’ H atoms resulting from the C_2H_2 dissociation [30]. A careful line shape

analysis of the measured H atom Doppler profiles (see [30]) revealed that no such ‘secondary’ H atoms were produced under the low photolysis laser intensity conditions of the present study. This finding further confirms that secondary photolysis processes did not affect our measurements.

3.2. H atom quantum yield in the Lyman- α photolysis of C_2H_2

To determine the absolute H atom quantum yield in the Lyman- α photolysis of C_2H_2 the photolysis of CH_4 was used as a calibrant. The photodissociation dynamics of CH_4 after excitation at the atmospherically important Lyman- α wavelength have been studied in detail (see e.g. [31–33] and references therein) and the H atom quantum yield $\phi_H(CH_4) = 0.47 \pm 0.11$ we reported in [32] has recently been confirmed by independent measurements [33].

For the evaluation of the C_2H_2 Lyman- α photolysis measurements the following expression was used [26]:

$$\Phi_H(121.6 \text{ nm}) = \gamma \left\{ \frac{S_H(C_2H_2) \phi_H(CH_4) \sigma_{CH_4} p_{CH_4}}{S_H(CH_4) \sigma_{C_2H_2} p_{C_2H_2}} \right\}, \quad (2)$$

where S_H stands for the integrated areas under the respective H atom Doppler profiles as shown in Fig. 3 and p_{CH_4} and $p_{C_2H_2}$ are the pressures of CH_4 and C_2H_2 , respectively. The CH_4 Lyman- α absorption cross-section $\sigma_{CH_4} = (2.0 \pm 0.2) \times 10^{-17} \text{ cm}^2$ was taken from [34], and the C_2H_2 Lyman- α absorption cross-section, $\sigma_{C_2H_2} = (7.6 \pm 0.1) \times 10^{-17} \text{ cm}^2$, was

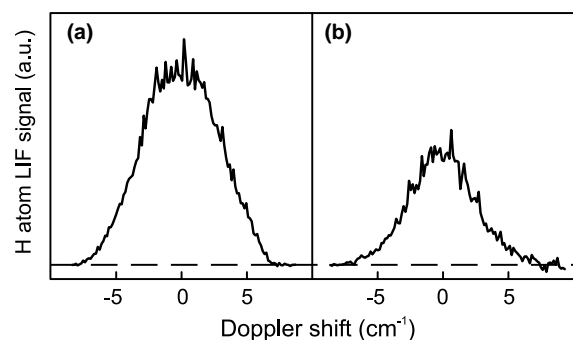


Fig. 3. H atom Doppler profiles measured in the Lyman- α (121.6 nm) photolysis of: (a) 9 mTorr of C_2H_2 and (b) 36 mTorr of CH_4 .

measured during the course of the present work in a similar way as described in [34]. γ represents a correction, which accounts for the different degree of absorption of the Lyman- α radiation by CH_4 and C_2H_2 . Nineteen independent calibration runs were performed which resulted in an average value of $\Phi_H(121.6 \text{ nm}) = 1.04 \pm 0.16$ for the H atom yield in the Lyman- α photolysis of C_2H_2 .

Absorption of a Lyman- α photon ($\hbar\omega_{L_\alpha} \approx 82236.8 \text{ cm}^{-1}$) leads to the excitation of the $3R''2_0^1$ Rydberg state of C_2H_2 with an excited-state lifetime of about 58 fs, for which the formation of H atoms along with C_2H radicals in the \tilde{X} electronic ground state and its first electronically excited \tilde{A} state (with virtually no indications for the formation of \tilde{B} state fragments) was demonstrated [18]. Because at this photolysis wavelength the H atom formation channel, $C_2 + H + H$ ($D_0 \approx 85\,500 \text{ cm}^{-1}$ [35]), is energetically not accessible, a H atom quantum yield of unity as obtained in the present study together with the results of Loffler et al. [18] implicates that the $H + C_2H(\tilde{X}^2\Sigma^+)/C_2H(\tilde{A}^2\Pi)$ channels are the only primary photodissociation channels which need to be considered in the modeling of the atmospheric Lyman- α photochemistry of C_2H_2 .

4. Summary

The dissociation dynamics of C_2H_2 after photoexcitation at 193.3 nm and at the Lyman- α wavelength (121.6 nm) was studied under collision-free conditions. Absolute quantum yields for H atom formation of $\Phi_H(193.3 \text{ nm}) = 0.94 \pm 0.12$ and $\Phi_H(121.6 \text{ nm}) = 1.04 \pm 0.16$ were obtained, demonstrating that for both photolysis wavelengths it is the formation of H atoms along with C_2H radicals which dominates the primary C_2H_2 photochemistry rather than the formation of ‘nonreactive’ electronically excited metastable acetylene and/or vinylidene as it was tentatively suggested in previous studies [4–11].

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) via SFB 359 at the

University Heidelberg. The stay of K.S.L. at the University Heidelberg was supported by KAIST (Korea). R.K.V. thanks DLR Bonn for a four months fellowship under the Indo-German bilateral agreement (Proj. No. IND 99/050). A.L. was supported by the Landesgraduierten Forderung Baden-Wurttemberg. H.R.V. and R.K.V. thank Prof. Y.T. Lee for encouraging comments and very fruitful discussion during the 3rd Asian Photochemistry Conference (January 2002, Mumbai, India), Prof. S. Rosenwaks and Dr. I. Bar for helpful communications, and Prof. J. Wolfrum for his continuous interest in the present work.

References

- [1] J. Warnatz, U. Maas, R.W. Dibble, *Combustion*, Springer, Heidelberg, 1996.
- [2] N.S. Smith, M.-C. Gazeau, A. Khelifi, F. Raulin, *Planet. Space Sci.* 47 (1999) 3.
- [3] R.P. Wayne, *Chemistry of Atmospheres*, Oxford Science Publications, Oxford, 1991.
- [4] S. Satyapal, R. Bersohn, *J. Phys. Chem.* 95 (1991) 8004.
- [5] K.S. Shin, J.V. Michael, *J. Phys. Chem.* 95 (1991) 5864.
- [6] K. Seki, H. Okabe, *J. Phys. Chem.* 97 (1993) 5284.
- [7] H. Okabe, *J. Chem. Phys.* 78 (1983) 1312.
- [8] H. Okabe, *J. Chem. Phys.* 75 (1981) 2772.
- [9] L.J. Stief, V.J. DeCarlo, R.J. Mataloni, *J. Chem. Phys.* 42 (1965) 3113.
- [10] M.P. Irion, K.L. Kompa, *Appl. Phys. B* 27 (1982) 183.
- [11] A.H. Laufer, *J. Photochem.* 27 (1984) 267.
- [12] A.M. Wodtke, Y.T. Lee, *J. Phys. Chem.* 89 (1985) 4744.
- [13] B.A. Balko, J. Zhang, Y.T. Lee, *J. Chem. Phys.* 94 (1991) 7958.
- [14] D.H. Mordaunt, M.N.R. Ashfold, R.N. Dixon, P. Loffler, L. Schnieder, K.-H. Welge, *J. Chem. Phys.* 108 (1998) 519.
- [15] N. Hashimoto, N. Yonekura, T. Suzuki, *Chem. Phys. Lett.* 264 (1997) 545.
- [16] J. Zhang, C.W. Riehn, M. Dulligan, C. Wittig, *J. Chem. Phys.* 103 (1995) 6815.
- [17] T. Arusi-Parpar, R.P. Schmid, Y. Ganot, I. Bar, S. Rosenwaks, *Chem. Phys. Lett.* 287 (1998) 347.
- [18] P. Loffler, E. Wrede, L. Schnieder, J.B. Halpern, W.M. Jackson, K.-H. Welge, *J. Chem. Phys.* 109 (1998) 5231.
- [19] L.-H. Lai, D.-C. Che, K. Liu, *J. Phys. Chem.* 100 (1996) 6376.
- [20] J.-H. Wang, Y.-T. Hsu, K. Liu, *J. Phys. Chem.* 101 (1997) 6593.
- [21] R.A. Brownsword, M. Hillenkamp, T. Laurent, R.K. Vatsa, H.-R. Volpp, *J. Chem. Phys.* 106 (1997) 4436.
- [22] R.A. Brownsword, T. Laurent, M. Hillenkamp, R.K. Vatsa, H.-R. Volpp, *J. Chem. Phys.* 106 (1997) 9563.
- [23] F. Shokoohi, T.A. Watson, H. Reisler, F. Kong, A.M. Renlund, C. Wittig, *J. Phys. Chem.* 90 (1986) 5695.
- [24] G. Hilbert, A. Lago, R. Wallenstein, *J. Opt. Soc. Am. B* 4 (1987) 1753.
- [25] J.P. Marangos, N. Shen, H. Ma, M.H.R. Hutchison, J.P. Connerade, *J. Opt. Soc. Am. B* 7 (1990) 1254.
- [26] R.A. Brownsword, M. Hillenkamp, T. Laurent, H.-R. Volpp, J. Wolfrum, R.K. Vatsa, H.-S. Yoo, *J. Chem. Phys.* 107 (1997) 779.
- [27] Y. Mo, K. Tonokura, Y. Masum, M. Kawasaki, T. Sato, T. Arikawa, P.T.A. Reilly, Y. Xie, Y. Yag, Y. Huang, R.J. Gordon, *J. Chem. Phys.* 97 (1992) 4815.
- [28] H. Okabe, *J. Chem. Phys.* 62 (1975) 2782.
- [29] A.M. Mebel, M. Hayashi, W.M. Jackson, J. Wrobel, M. Green, D. Xu, S.H. Lin, *J. Chem. Phys.* 114 (2001) 9821.
- [30] J. Segall, R. Lavi, Y. Wen, C. Wittig, *J. Phys. Chem.* 93 (1989) 7287.
- [31] A.J.R. Heck, R.N. Zare, D.W. Chandler, *J. Chem. Phys.* 104 (1996) 3399.
- [32] R.A. Brownsword, M. Hillenkamp, T. Laurent, R.K. Vatsa, H.-R. Volpp, J. Wolfrum, *Chem. Phys. Lett.* 266 (1997) 259.
- [33] J.-H. Wang, K.P. Liu, Z. Min, H. Su, R. Bersohn, J. Preses, J.Z. Larese, *J. Chem. Phys.* 113 (2000) 4146.
- [34] R.K. Vatsa, H.-R. Volpp, *Chem. Phys. Lett.* 340 (2001) 289.
- [35] Y.-C. Hsu, M.-S. Lin, C.-P. Hsu, *J. Chem. Phys.* 94 (1991) 7832.