(ν(NH)), 2971 (s), 2865 (s, sh), 2855 (s, sh), 2834 (s), 2786 (s; $5 \times \nu(CH_3)$), 1171 (s), 987 cm^{-1} (s); MS (EI): m/z (%): 393 (20) [M^+], 349 (20) [$M^+ - N(CH_3)_2$], 303 (100) [$M^+ - 2N(CH_3)_2$].

Crystal structure analysis of **2**: Crystals of **2** were grown from pentane at -40 °C, crystal dimensions $0.63 \times 0.24 \times 0.11$ mm; $\lambda = 0.71073$ Å; crystallographic data at 100 K: triclinic, space group $P\bar{1}$ (no. 2); $a = 832.83(17)$, $b = 1069.0(2)$, $c = 1408.3(3)$ pm; $\alpha = 69.62(3)$, $\beta = 74.95(3)$, $\gamma = 69.41(3)°$; $V = 1.0867(4)$ nm^3; $Z = 2$; $\rho_{calcd} = 1.203$ Mg m^{-3}; $F(000) = 432$; $\mu(Mo_{K\alpha}) = 0.234$ mm^{-1}. Data were collected on a Bruker AXS SMART-CCD-System with ω scans. Of 13602 reflections collected ($4.24° < 2\theta > 55.04°$), 4891 were independent ($R_{int} = 0.0622$). The structure was solved by direct methods (SHELXS-97[22]) and refined by full-matrix least squares on F^2 using 241 parameters ($R(F) \geq 4\sigma(F) = 0.0470$, $wR2 = 0.1328$); max./min. residual electron density $0.728/-0.571$ e Å^{-3}. Hydrogen atoms were located from the difference Fourier map, all methyl hydrogen atoms were constrained to idealized positions, and imido hydrogen atoms were refined freely. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-112321. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Silicon imide gel preparation by ammonolysis of **1** and **2**: To a solution of **1** (2.5 g, 14.2 mmol) in dry THF (100 mL) in a 250-mL round-bottomed glass flask was added trifluoromethanesulfonic acid (12 μL, 0.14 mmol, 1 mol%). On warming to 50 °C evolution of gaseous dimethylamine was observed. After 18 h analysis by IR and MS showed complete conversion of **1** into **2** (ca. 80%) and other unidentified by-products (ca. 20%). A solution of ammonia (42 mmol) in dry THF (40 mL) was added, and the mixture was left quiescent at 50 °C for 18 h, at which point a slight opalescence was observed. Addition of further ammonia (14 mmol) resulted in rapid gelation to give, after several minutes, a translucent rigid gel filling the original volume of the reaction mixture. Evaporation of the solvent and dimethylamine in a stream of argon followed by drying under reduced pressure at 50 °C for 10 h yielded a translucent white solid. IR (KBr): $\tilde{\nu} = 3475$ (w, sh; ($\nu(NH_2)$)), 3362 (m; ν(NH)), 2973 (m), 2863 (m, sh), 2857 (m, sh), 2835 (m), 2787 (m; $\nu(CH_3)$), 1551 (w; $\delta(NH_2)$), 1181 (s), 985 cm^{-1} (s).

Received: December 17, 1998 [Z12793IE]
German version: *Angew. Chem.* **1999**, *111*, 2073–2076

Keywords: ammonolysis · ceramics · nitrides · sol–gel processes

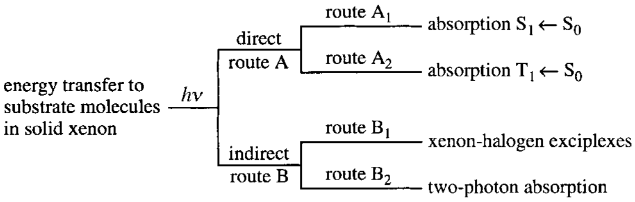
---

[1] *Better Ceramics Through Chemistry, Vol. I and II* (Eds.: C. J. Brinker, D. E. Clark, D. R. Ulrich), Materials Research Society, Pittsburgh, **1984**.
[2] C. J. Brinker, G. W. Scherer, *Sol-Gel Science*, Academic Press, San Diego, **1990**.
[3] R. Riedel, E. Kroke, A. Greiner, A. O. Gabriel, L. Ruwisch, J. Nicolich, P. Kroll, *Chem. Mater.* **1998**, *10*, 2964.
[4] C. K. Narula, R. T. Paine, R. Schaeffer, *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 383.
[5] M. Siebold, C. Rüssel, *Mater. Res. Soc. Symp. Proc.* **1988**, *121*, 477.
[6] A. O. Gabriel, R. Riedel, *Angew. Chem.* **1997**, *109*, 371; *Angew. Chem. Int. Ed. Engl.* **1997**, *34*, 384.
[7] A. O. Gabriel, R. Riedel, S. Storck, W. F. Maier, *Appl. Organomet. Chem.* **1997**, *11*, 833.
[8] W. Schnick, *Angew. Chem.* **1993**, *105*, 846; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 806.
[9] T. Schlieper, W. Schnick, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1037.
[10] W. Schnick, H. Huppertz, *Chem. Eur. J.* **1997**, *3*, 679.
[11] R. E. King; B. Kammer, P. Hopper, C. L. Schilling (Union Carbide Corp.), US-A 4,675,424, **1987**.
[12] M. Jansen, J. Löffelholtz, *Adv. Mater.* **1992**, *4*, 746.
[13] O. Wagner, M. Jansen, H.-P. Baldus, *Z. Anorg. Allg. Chem.* **1994**, *620*, 366.
[14] J. Hapke, G. Ziegler, *Adv. Mater.* **1995**, *7*, 380.
[15] M. Jansen, H.-P. Baldus, O. Wagner (Bayer AG), EP-A 502399A2, **1992**.
[16] N. Percheneck, H.-P. Baldus, J. Löffelholtz, M. Jansen (Bayer AG), EP-A 623643, **1994**.
[17] R. G. Gordon, D. M. Hoffman, U. Riax, *Chem. Mater.* **1990**, *2*, 480.
[18] A referee has pointed out to us the previous preparation of tris(trimethylsilylamido)silylamine: K. A. Andrianov, M. M. Il'in, V. N. Talanov, I. I. Zhuraskovskaya, *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1976**, *25*, 2432.
[19] J. Desmaison, D. Giraud, M. Billy, *Rev. Chim. Miner.* **1972**, *9*, 417.
[20] U. Wannagat, P. Schmidt, M. Schulze, *Angew. Chem.* **1967**, *79*, 409; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 446.
[21] U. Wannagat, M. Schulze, *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 789.
[22] a) G. M. Sheldrick, SHELXS-97, Program for the solution of crystal structures, Universität Göttingen, **1997**; b) G. M. Sheldrick, SHELXL-97, Program for structure refinement, Universität Göttingen, **1997**.

Solid Xenon: A Medium for Unusual Photoreactions**

Günther Maier* and Christian Lautz

As is shown in this communication, a molecule isolated in a xenon matrix at 10 K can react upon irradiation depending on the conditions by four, in principle different mechanisms (Scheme 1). Of course, as in any other transparent medium a substance absorbing in the wavelength region of the irradiating light can be induced to undergo a photoreaction also in a xenon matrix ($S_1 \leftarrow S_0$ absorption; direct route A_1). For instance, matrix irradiation ($\lambda = 313$ nm) of 2-diazo-2*H*-imidazole in argon as well as in xenon leads to 2*H*-imidazol-2-ylidene.[1] In this case the special feature of xenon lies only in its ability to stabilize the generated carbene by complexation.[1]



Scheme 1. Possible photoexcitations of a substrate molecule in a xenon matrix.

Surprisingly, in a xenon matrix even those molecules are accessible for photoreactions, which cannot absorb light at the wavelength employed. This phenomenon can be observed when the xenon matrix is doped with halogen atoms (indirect route B_1).[2] Hereby the halogen atoms absorb the excitation energy, which is stored in xenon halogen exciplexes, whose

---

[*] Prof. Dr. G. Maier, Dipl.-Chem. C. Lautz
Institut für Organische Chemie der Universität
Heinrich-Buff-Ring 58, D-35392 Giessen (Germany)
Fax: (+49) 641-99-34309

[**] This work was supported by the Volkswagenstiftung, the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft.

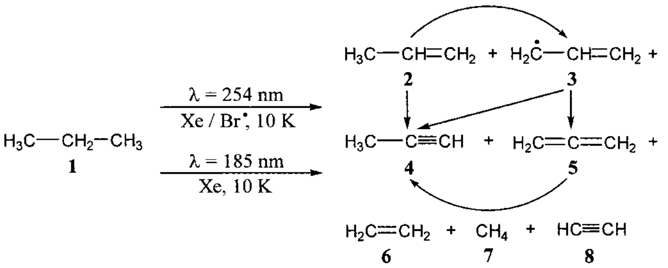
photophysics is well known.[3] Subsequently the stored excitation energy is transferred to the substrate molecules embedded in the matrix.

Another variant (indirect route B_2) is the two-photon excitation of the xenon using an excimer laser (KrF; $\lambda = 248$ nm). The excitons Xe_n^* generated by this procedure transfer their energy to the matrix-isolated molecules of the starting material resulting in their cleavage into smaller fragments.[2d, 4, 5]

Until now we have used three- and four-membered ring compounds in our studies on indirect excitation. Thus, it was an open question, whether the ring strain present in these molecules was a prerequisite for the bond cleavage. Propane (**1**) was considered as test molecule, first, because it possesses no strain energy, second, a direct $S_1 \leftarrow S_0$ excitation at a wavelength longer than 170 nm should not be possible, and third, the expected products generated by a C–H or C–C bond cleavage, initiated by the indirect photoexcitation, should easily be identified by comparison with their known matrix spectra. The results reported herein not only prove that indirect photofragmentation following the pathways B_1 and B_2 also occurs in strain-free open-chain hydrocarbons, but also another important observation was made: Propane (**1**) is even fragmented when for the irradiation in undoped xenon the 185 nm line of a low-pressure mercury lamp is used instead of a KrF laser. This direct fragmentation is observed in spite of the fact that under the applied conditions a $S_1 \leftarrow S_0$ transition (route A_1) can be excluded. Thus we assume that in solid xenon an additional reaction channel exists, presumably a direct $T_1 \leftarrow S_0$ excitation (route A_2), which is promoted by the heavy atom effect of xenon and results finally in bond cleavage.

*Irradiation of **1** in a $Br^{\bullet}$-doped xenon matrix (route B_1)*: Propane (**1**) is photostable in an argon matrix doped with bromine atoms when light of the wavelength $\lambda = 254$ nm is employed. However, if a $Br^{\bullet}$-doped xenon matrix is used instead, nearly 50% of the molecules of **1** have reacted after irradiation for 47 h at the same wavelength. The products of this photolysis are propene (**2**), the allyl radical (**3**), propyne (**4**), allene (**5**), ethene (**6**), methane (**7**), and acetylene (**8**) (Scheme 2, Table 1). In addition the bands of the cation Xe_2H^+[6] (730.9, 843.0, and 951.7 cm^{-1}), which is formed from exciplex $Xe_2^{\bullet+}X^-$ by addition of a H atom, can be registered.

During the photolysis the products of the primary steps can clearly be differentiated from those of the secondary steps. The first detectable molecules originating from the C–H bond cleavage of **1** are propene (**2**) and the allyl radical (**3**), whose signals appear simultaneously in the spectrum. At a later stage of the photolysis the secondary products of **2** and **3**, namely propyne (**4**) and allene (**5**), can be detected. This course of the photolysis corresponds with experiments with separately studied samples of **2** and **5** in a halogen-doped xenon matrix: Propene (**2**) yields upon irradiation with light of the wavelength $\lambda = 254$ nm besides **3** also **4** and **5**, whereas **5** slowly isomerizes to the thermodynamically more stable propyne (**4**).[7]



Scheme 2. Photolysis of **1** in a xenon matrix.

Table 1. Band positions ([cm^{-1}]; relative intensities in parentheses; vw = very weak, w = weak, m = middle, s = strong, vs = very strong) and assignment of the products upon photolysis of **1**. First column: Irradiation in a $Br^{\bullet}$-doped xenon matrix with $\lambda = 254$ nm (route B_1). Second column: Irradiation in a xenon matrix with laser light (KrF; $\lambda = 248$ nm; route B_2). Third column: Irradiation in a xenon matrix with a Hg lamp ($\lambda = 185$ nm; route A_2).

Route B_1	Route B_2	Route A_2	Assignment
626.8 (m)	–	626.8 (m)	**4**
727.7 (s)	727.7 (m)	727.7 (s)	**8**
798.5 (s)	798.5 (s)	798.5 (w)	**3**
834.9 (m)	–	834.9 (vw)	**5**
ca. 910 (br., s)	ca. 910 (br., s)	905.9 (w)	**2**
947.9 (m)	947.9 (w)	947.9 (vw)	**6**
971.0 (m)	971.0 (w)	971.0 (vw)	**3**
988.4 (m)	988.4 (w)	988.4 (vw)	**2**
1300.2 (vs)	1300.2 (m)	1300.2 (s)	**7**
1317.2 (w)	–	1317.2 (w)	**8**
1432.9 (s)	1432.9 (m)	1432.9 (w)	**6**
1448.5 (m)	1448.5 (m)	1448.5 (vw)	**2**
ca. 1955 (br., w)	–	–	**5**
2978.0 (m)	–	–	**6**
3007.5 (s)	–	–	**7**
3094.5 (m)	–	–	**6**
3265.1 (m)	–	–	**8**

The primarily detectable products of the simultaneously occurring C–C bond cleavage of **1** are ethene (**6**) and methane (**7**). Practically at the same time also the signals of acetylene (**8**), which is a secondary product of **6**, begin to rise. At no stage of the photolysis are signals of methyl and ethyl radicals[8] measured. However, this is no surprise since both radicals are formed wthin the same matrix cage and can undergo either a back-reaction to **1** or secondary reactions such as the disproportionation into **6** and **7**.

This finding indicates that upon irradiation in a $Br^{\bullet}$-doped xenon matrix the fragmentation of **1** can follow two reaction channels, a primary C–H or C–C bond cleavage. Since a direct absorption of the applied energy ($\lambda = 254$ nm; $E = 112.6$ kcal mol^{-1}) by the hydrocarbon **1** (no absorption band in this region) is not possible, the energy of irradiation has to be absorbed by the halogen atoms isolated in the solid xenon and is stored in the already mentioned xenon–halogen exciplexes.[3] The mechanism of the energy transfer to the substrate molecules and the details of the bond cleavage still need to be verified. Besides a charge-transfer complex with holes in the valence band of solid xenon[2] also radical cations have to be discussed as potential intermediates. An estimate (Born equation) of the effect of the $Br^{\bullet}$-doped xenon matrix on the ionization energy of **1** gives a strongly reduced value of $I_{\text{matrix}} \approx 5.4$ eV $= 124.5$ kcal mol^{-1} ($I_{\text{gas phase}} = 10.95$ eV $= 252.5$ kcal mol^{-1}[9]). That is, this estimated value for the reduced ionization energy approximates the used irradiation energy. The geometry of the radical cation of **1** is known from ESR experiments.[10] One of the two C–C bonds and one of the primary C–H bonds are considerably lengthened. The thermal chemistry of the radical cation of **1**, for instance the formation of the 1-propyl radical,[11] can be explained by this change in geometry. We found no experimental evidence for the intermediacy of the radical cation of **1** in our experiments. Nevertheless, it cannot be excluded that upon irradiation of **1** in a Br$^\bullet$-doped xenon matrix the obseved bond cleavages occur via the radical cation.[12]

*Irradiation of **1** in a xenon matrix with laser light (route B_2)*: Propane (**1**) is photostable in an argon matrix upon irradiation with light of the wavelengths $\lambda = 254$ nm and $\lambda = 185$ nm. However, if a xenon matrix is applied in combination with an excimer laser (KrF; $\lambda = 248$ nm) as the light source **1** undergoes a slow photoreaction (10% transformation after 10 h photolysis). The main products of this photolysis, namely propene (**2**) and allyl radical (**3**), originate from the C–H bond cleavage. Propyne (**4**) and allene (**5**) are not formed under these conditions of irradiation (Table 1). The C–C cleavage of **1** plays only a minor role upon laser excitation, as can be documented by the observation that the concentrations of **6**–**8** are smaller than in the case of the irradiation in a Br$^\bullet$-doped xenon matrix. The photolability of **1** upon usage of a laser can be explained by the two-photon mechanism mentioned above.[2d, 4, 5]

*Irradiation of **1** in an undoped xenon matrix with a Hg low-pressure lamp (route A_2)*: The most astonishing observation is that **1** reacts in a xenon matrix—but not in an argon matrix—even in the absence of halogen atoms with light of the wavelength $\lambda = 185$ nm of a mercury low-presssure lamp (with interference filter). Owing to the low photon density a two-photon process can be excluded under these conditions.

The products **2**–**6** of this photolysis (Figure 1, Table 1) are the same as those in the experiments in the doped matrix, but the relative concentrations differ. An additional intense signal at $\tilde{\nu} = 2023.9\ \text{cm}^{-1}$ can be assigned to the cumulenic carbon species C_3.[13] Figure 1 shows the difference spectrum after the photolysis of **1** with light of the wavelength $\lambda = 185$ nm for 45.5 h. After this period of irradiation 20% of the starting material had reacted. During this irradiation the products of the C–C bond cleavage, **7** and **8**, clearly prevail. Presumably the photochemically induced reaction steps are similar to those for the irradiation in a Br$^\bullet$-doped matrix (see above). That means, the primary products are methane (**7**) and ethene (**6**), which is subsequently dehydrogenated to acetylene (**4**).[14]

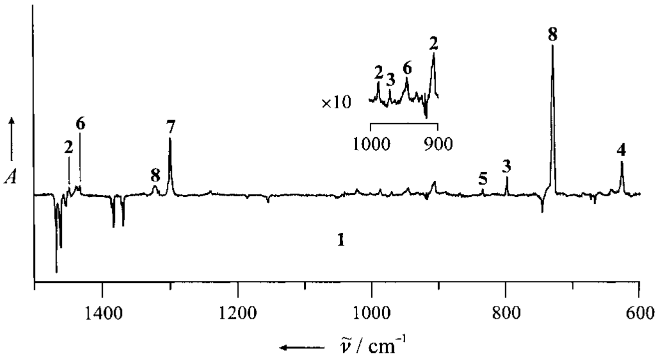


Figure 1. Difference spectrum after 45.5 h photolysis of **1** in a xenon matrix with light of the wavelength $\lambda = 185$ nm. IR bands with negative values diminish, while those with positive values are formed during irradiation.

Surprising about the fragmentation of **1** in a xenon matrix by irradiation with light of the wavelength $\lambda = 185$ nm is the fact that the reaction occurs at all—after all, **1** is photostable in an argon matrix under the same conditions. A comparison with the gas phase UV spectrum of **1**[15] and the spectrum of a film of solid **1**[16] shows that the long wavelength edge of the absorption lies at $\lambda \approx 160$ nm. The observed reaction also cannot originate from a direct $S_1 \leftarrow S_0$ absorption (route A_1). Even if one assumes a bathochromic shift of the absorption cut-off of $\Delta\lambda \approx +10$ nm, which we have observed in other studies for instance for 1,3-butadiene and trimethylamine upon a change of the matrix material from argon to xenon, a direct $S_1 \leftarrow S_0$ absorption is unlikely. In addition one has to realize that under the applied matrix conditions an energy transfer by a triplet sensitizer can be excluded.

Evidently the use of xenon as matrix material causes a change in the absorption behavior. It is known[17, 18] that due to the heavy atom effect the course of a photochemical reaction can be influenced by the choice of xenon as the matrix material. After direct absorption ($S_1 \leftarrow S_0$) of the irradiating light an intersystem crossing, favored by xenon, can occur, and thus a different mechanism—compared to reactions in usual matrix materials (e. g. argon or nitrogen)—becomes possible.

Xenon also has an influence on the lifetime of the phosphorescence of embedded substrate molecules. For benzene it amounts to 16 s in argon, but to only 0.07 s in xenon.[19] The external heavy atom effect enhances the rate of the $T_1 \rightarrow S_0$ transition. There are even examples for a direct entry to the T_1-hypersurface by absorption of a molecule isolated in a xenon matrix. For instance, the forbidden $T_1 \leftarrow S_0$ transition of α-chloronaphthalene can be measured directly in the presence of xenon under high pressure. This absorption only becomes measurable by the spin-orbit interaction with the external heavy atom xenon.[20] A direct $T_1 \leftarrow S_0$ absorption can also have chemical consequences: Irradiation of *cis*- or *trans*-1,2-dichloroethene in a xenon matrix with light of the wavelength $\lambda > 300$ nm results in an isomerization of the respective alkene,[21] in spite of the fact that these molecules show no $S_1 \leftarrow S_0$ absorption in the range of the irradiating light. On the other hand, the $T_1 \leftarrow S_0$ transition of the chloroethenes lies at 300–400 nm (measured in the presence of oxygen[22]).

We assume that upon irradiation of **1** in a xenon matrix with light of the wavelength $\lambda = 185$ nm a direct $T_1 \leftarrow S_0$ excitation can similarly be achieved by the external heavy atom effect of xenon. Former calculations[23] on the excited states of **1** indicate that the triplet states should lie not much (0.15–0.30 eV) below the singlet states. In a pure saturated hydrocarbon a $\sigma^* \leftarrow \sigma$ excitation leads to a dissociative Rydberg state. Starting from such an excited state the detected fragmentation reactions can be explained easily.

Conclusion: A bond cleavage by indirect irradiation of the substrate molecule in a halogen-doped xenon matrix (route B_1) is even possible in strain-free open-chain hydrocarbons.

Moreover, the fragmentation of matrix-isolated molecules can be achieved by using the heavy atom effect of xenon (route A_2).

Received: January 22, 1999 [Z12947IE]
German version: *Angew. Chem.* **1999**, *111*, 2118–2121

Keywords: halogens · matrix isolation · photochemistry · xenon

[1] G. Maier, J. Endres, *Chem. Eur. J.* **1999**, *5*, 1590–1597.
[2] a) G. Maier, H. P. Reisenauer, K. Lanz, R. Troß, D. Jürgen, B. A. Hess, Jr., L. J. Schaad, *Angew. Chem.* **1993**, *105*, 119–121; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 74–76; b) G. Maier, D. Jürgen, R. Troß, H. P. Reisenauer, B. A. Hess, Jr., L. J. Schaad, *Chem. Phys.* **1994**, *189*, 383–399; c) G. Maier, S. Senger, *Angew. Chem.* **1994**, *106*, 605–606; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 558–559; d) G. Maier, S. Senger, *Liebigs Ann.* **1996**, 45–47; e) G. Maier, S. Senger, *J. Am. Chem. Soc.* **1997**, *119*, 5857–5861; f) G. Maier, A. Bothur, *Eur. J. Org. Chem.* **1998**, 2063–2072.
[3] a) M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1986**, *85*, 5660–5681; b) M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1988**, *89*, 4102–4123; c) M. E. Fajardo, V. A. Apkarian, *J. Chem. Phys.* **1988**, *89*, 4124–4136.
[4] W. G. Lawrence, V. A. Apkarian, *J. Chem. Phys.* **1992**, *97*, 6199–6207.
[5] G. Maier, C. Lautz, *Eur. J. Org. Chem.* **1998**, 769–776.
[6] a) H. M. Kunttu, J. A. Seetula, M. Räsänen, V. A. Apkarian, *J. Chem. Phys.* **1992**, *96*, 5630–5635; b) H. M. Kunttu, J. A. Seetula, *Chem. Phys.* **1994**, *189*, 273–292.
[7] S. Senger, Diplomarbeit, Universität Gießen, **1993**.
[8] J. Pacansky, M. Dupuis, *J. Am. Chem. Soc.* **1982**, *104*, 415–421.
[9] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. Ref. Data Suppl. 1* **1988**, *17*, 127.
[10] K. Toriyama, M. Okazaki, K. Nunome, *J. Chem. Phys.* **1991**, *95*, 3955–3963.
[11] K. Toriyama, K. Nunome, M. Iwasaki, *J. Chem. Phys.* **1982**, *77*, 5891–5912.
[12] Concerning investigations in argon matrices see: T. Bally, *Chimia* **1994**, *48*, 378–386.
[13] A. Lakhlifi, R. Dahoo, M. Vala, J. Szczepanski, S. Ekern, *Chem. Phys.* **1997**, *222*, 241–257.
[14] P. Borrell, A. Cervenka, J. W. Turner, *J. Chem. Soc. B* **1971**, 2293–2298.
[15] J. W. Raymonda, W. T. Simpson, *J. Chem. Phys.* **1967**, *47*, 430–448.
[16] B. A. Lombos, P. Sauvageau, C. Sandorfy, *Chem. Phys. Lett.* **1967**, *1*, 382–384.
[17] S. T. Collins, G. C. Pimentel, *J. Phys. Chem.* **1984**, *88*, 4258–4264.
[18] J. Lundell, M. Krajewska, M. Räsänen, *J. Phys. Chem. A* **1998**, *102*, 6643–6650.
[19] M. R. Wright, R. P. Frosch, G. W. Robinson, *J. Chem. Phys.* **1960**, *33*, 934–935.
[20] A. Grabowska, *Spectrochim. Acta* **1963**, *19*, 307–313.
[21] S. L. Laursen, G. C. Pimentel, *J. Phys. Chem.* **1989**, *93*, 2328–2333.
[22] Z. R. Grabowski, A. Bylina, *Trans. Faraday Soc.* **1964**, *60*, 1131–1136.
[23] A. Richartz, R. J. Buenker, S. Peyerimhoff, *Chem. Phys.* **1978**, *31*, 187–196.

Organic Quantum-Confined Structures through Molecular Layer Epitaxy**

Vladimir Burtman, Alexander Zelichenok, and Shlomo Yitzchaik*

Organic multilayered structures have attracted significant attention because they are potential substitutes for regular elemental components in electronic and electrooptic devices as well as excellent objects for experimental studies of basic quantum-mechanical models and principles of solid-state physics.[1] Novel layered structures of organic light emitting devices (OLEDs) were reported to exhibit three-color emission.[2] The study of organic field effect transistors (OFETs) fabricated from organic conjugated heterocyclic compounds has shown that an electron mobility as high as $1.3\,cm^2V^{-1}s^{-1}$ is achievable in molecular electronic devices.[3] Recently the first OLED- and OFET-integrated optoelectronic devices were reported.[4]

Multilayered structures such as self-assembled monolayers,[5] electrostatic polymer assemblies,[6] and Langmuir–Blodgett films,[7] can be obtained by solution-derived methods, whereas ultra high vacuum (UHV) deposition,[8] organic molecular beam epitaxy (OMBE),[9] and molecular layer deposition[10] were used for vapor-phase assembly of organic heterostructures. However, there is as yet no straightforward vapor-phase deposition method for assembling organic superlattices that enable epitaxial growth with covalent bonding. Inorganic atomic layer epitaxy (ALE)[11] is the main vapor-phase method that can be used to build covalently bonded epitaxial multilayers in a layer-by-layer fashion.

We developed a new method for deposition of organic multilayers, molecular layer epitaxy (MLE), which is based on four levels: deposition of a template layer, self-limiting, vapor-phase reactions, covalent ("*c* axis") interlayer bonding, and π stacking in the *xy* plane. A template layer is firstly deposited on an oxide surface, such as Si/SiO_2, quartz, or glass/indium tin oxide (ITO; Figure 1a, step 1), exposing propylamine functionalities toward the interface and in turn dictating epitaxial growth. We choose the siloxane coupling network to enhanced thermal stability. This coupling reaction on silicon's native oxide yields an ordered monolayer. However, on rougher surfaces such as ITO this reaction flattens the surface by a less controlled condensation reaction that can result in the assembly of two to three layers. Then discrete pulses of reactants, liquids or solids that undergo self-limiting reactions, are carried to the surface by an inert carrier gas in an MLE deposition reactor

---

[*] Dr. S. Yitzchaik, Dr. V. Burtman, Dr. A. Zelichenok
Department of Inorganic and Analytical Chemistry
The Hebrew University of Jerusalem
Jerusalem 91904 (Israel)
Fax: (+972)2-6585319
E-mail: sy@cc.huji.ac.il

[**] S.Y. acknowledges support for this research by the Israel Science Foundation (ISF; grant 651/95-2), the US–Israel Binational Science Foundation (BSF; grant 95-0085), and the Israel Academy of Science and Humanitarians. V.B. thanks the Berg Foundation for a postdoctoral fellowship.

1433-7851/99/3813-2041 $ 17.50+.50/0