The thermal and UV photo-induced decomposition of azomethane on Rh(111)†

Attila Kis, Robert Barthos and Janos Kiss*

Reaction Kinetics Research Group of the Hungarian Academy of Sciences, University of Szeged, H-6701 Szeged, P.O. Box 168, Hungary. E-mail: jkiss@chem.u-szeged.hu

Received 15th May 2000, Accepted 25th July 2000
Published on the Web 29th August 2000

The thermal and UV photo-induced decomposition of azomethane, CH₃N=NCH₃, was investigated by means of reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption spectroscopy (TPD). The RAIRS data revealed that azomethane adsorbs in the trans-configuration mode on Rh(111) at 90 K. During thermal treatment, azomethane decomposes exclusively by N-N bond scission, yielding H₂, N₂, C₂N₂ and traces of HCN. Upon UV irradiation at 90 K, adsorbed azomethane undergoes tautomerization, forming formaldehyde methylhydrazone, CH₃NHN=CH₂. The important features of the post-irradiation TPD spectra are the significant suppression of C₂N₂ and N₂ formation, and the appearance of the new products methylamine (CH₃NH₂) and CH₄. C-N bond scission also occurred in the illuminated chemisorbed layer at 90 K.

1 Introduction

Azomethane (CH₃N=NCH₃) is an interesting molecule. Its thermal decomposition in the gas phase produces CH₃ radicals and N₂ by C-N bond cleavage. This provides a convenient method for the preparation of CH₃ adsorbed on solid surfaces and study of its surface chemistry. On most metal surfaces, however, the primary process is the rupture of the N-N bond. It appears that the bonding of azomethane on certain surfaces allows a new decomposition pathway. C-N bond dissociation is induced by electronic excitation, such as the electron-induced decomposition of azomethane on Ag(111) and the UV photolysis of azomethane condensed on Pd(111). A study of the interactions of C₂N₂ with metal surfaces demonstrated that the behaviour of Rh towards the CN group is basically different from that of Ag, Cu and Ni, as at high temperature it induces C-N bond cleavage to give adsorbed N and C. Rh also exhibits outstanding reactivity as compared to Cu in C-N bond breaking in the NCO surface complex.

In the light of the above findings, it appeared interesting to explore whether the high reactivity of Rh(111) towards the C-N bond is also exhibited in the decomposition of azomethane. A recent high-resolution electron energy loss spectroscopy (HREELS) study found that azomethane adsorbs molecularly in the trans-configuration on Rh(111) at 100 K, and dissociates exclusively via N-N bond scission above 300 K. Preadsorbed oxygen inhibits N-N bond breaking, leading to the C-N bond dissociation. The present paper reports on the use of combined RAIRS (with its better resolution) and TPD to acquire more information on the adsorption modes at 90 K, and on the bond rearrangement on a clean surface in the low-temperature range. It was found that UV light illumination alters the adsorption mode and chemistry of azomethane on Rh(111).

2 Experimental

The experiments were performed in a two-level UHV system with a background pressure of 5 × 10⁻¹⁰ mbar. The lower part of the chamber had facilities for Auger electron spectroscopy (AES) and TPD. The upper part was equipped with a single-beam Fourier-transform IR spectrometer (Mattson Research Series), which was used for the RAIRS experiments. All IR spectra were averaged over 512 scans using an MCT detector at 2-4 cm⁻¹ resolution. Sample spectra were related to a background taken immediately after the sample scan by flashing the crystal to 1300 K. The scan was initiated after the crystal temperature had returned to 90 K.

The Rh(111) single-crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1-2 kV, 1 × 10⁻⁴ Pa argon, 3 μA) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The sample was heated resistively, and the temperature was measured with a chromel-alumel thermocouple. The typical heating rate for TPD was 4 K s⁻¹. Azomethane was synthesized according to the procedure described by Renaud and Leitch. The product was purified by several freeze-pump-thaw cycles before each day of the experiments. No impurities were detected with a quadrupole mass spectrometer. However, it was difficult to determine whether the small increase in the H₂O peak (18 u) was due to a rise in the background or was an impurity in the azomethane. Azomethane was dosed through a multicapillary doser. The delivered to the crystal at full arc was about 100 mW cm⁻².

The incident power flux was initiated after the crystal temperature had returned to 90 K.

The Rh(111) single-crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1-2 kV, 1 × 10⁻⁴ Pa argon, 3 μA) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The sample was heated resistively, and the temperature was measured with a chromel-alumel thermocouple. The typical heating rate for TPD was 4 K s⁻¹. Azomethane was synthesized according to the procedure described by Renaud and Leitch. The product was purified by several freeze-pump-thaw cycles before each day of the experiments. No impurities were detected with a quadrupole mass spectrometer. However, it was difficult to determine whether the small increase in the H₂O peak (18 u) was due to a rise in the background or was an impurity in the azomethane. Azomethane was dosed through a multicapillary doser. The delivered to the crystal at full arc was about 100 mW cm⁻².

The incident power flux was initiated after the crystal temperature had returned to 90 K.

The Rh(111) single-crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1-2 kV, 1 × 10⁻⁴ Pa argon, 3 μA) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The sample was heated resistively, and the temperature was measured with a chromel-alumel thermocouple. The typical heating rate for TPD was 4 K s⁻¹. Azomethane was synthesized according to the procedure described by Renaud and Leitch. The product was purified by several freeze-pump-thaw cycles before each day of the experiments. No impurities were detected with a quadrupole mass spectrometer. However, it was difficult to determine whether the small increase in the H₂O peak (18 u) was due to a rise in the background or was an impurity in the azomethane. Azomethane was dosed through a multicapillary doser. The delivered to the crystal at full arc was about 100 mW cm⁻².

The incident power flux was initiated after the crystal temperature had returned to 90 K.

The Rh(111) single-crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1-2 kV, 1 × 10⁻⁴ Pa argon, 3 μA) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The sample was heated resistively, and the temperature was measured with a chromel-alumel thermocouple. The typical heating rate for TPD was 4 K s⁻¹. Azomethane was synthesized according to the procedure described by Renaud and Leitch. The product was purified by several freeze-pump-thaw cycles before each day of the experiments. No impurities were detected with a quadrupole mass spectrometer. However, it was difficult to determine whether the small increase in the H₂O peak (18 u) was due to a rise in the background or was an impurity in the azomethane. Azomethane was dosed through a multicapillary doser. The delivered to the crystal at full arc was about 100 mW cm⁻².

The incident power flux was initiated after the crystal temperature had returned to 90 K.

The Rh(111) single-crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1-2 kV, 1 × 10⁻⁴ Pa argon, 3 μA) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The sample was heated resistively, and the temperature was measured with a chromel-alumel thermocouple. The typical heating rate for TPD was 4 K s⁻¹. Azomethane was synthesized according to the procedure described by Renaud and Leitch. The product was purified by several freeze-pump-thaw cycles before each day of the experiments. No impurities were detected with a quadrupole mass spectrometer. However, it was difficult to determine whether the small increase in the H₂O peak (18 u) was due to a rise in the background or was an impurity in the azomethane. Azomethane was dosed through a multicapillary doser. The delivered to the crystal at full arc was about 100 mW cm⁻².

The incident power flux was initiated after the crystal temperature had returned to 90 K.

The Rh(111) single-crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1-2 kV, 1 × 10⁻⁴ Pa argon, 3 μA) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The sample was heated resistively, and the temperature was measured with a chromel-alumel thermocouple. The typical heating rate for TPD was 4 K s⁻¹. Azomethane was synthesized according to the procedure described by Renaud and Leitch. The product was purified by several freeze-pump-thaw cycles before each day of the experiments. No impurities were detected with a quadrupole mass spectrometer. However, it was difficult to determine whether the small increase in the H₂O peak (18 u) was due to a rise in the background or was an impurity in the azomethane. Azomethane was dosed through a multicapillary doser. The delivered to the crystal at full arc was about 100 mW cm⁻².

The incident power flux was initiated after the crystal temperature had returned to 90 K.

The Rh(111) single-crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1-2 kV, 1 × 10⁻⁴ Pa argon, 3 μA) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The sample was heated resistively, and the temperature was measured with a chromel-alumel thermocouple. The typical heating rate for TPD was 4 K s⁻¹. Azomethane was synthesized according to the procedure described by Renaud and Leitch. The product was purified by several freeze-pump-thaw cycles before each day of the experiments. No impurities were detected with a quadrupole mass spectrometer. However, it was difficult to determine whether the small increase in the H₂O peak (18 u) was due to a rise in the background or was an impurity in the azomethane. Azomethane was dosed through a multicapillary doser. The delivered to the crystal at full arc was about 100 mW cm⁻².

The incident power flux was initiated after the crystal temperature had returned to 90 K.
The temperature rise of the crystal during irradiation did not exceed 5 K.

3 Results and discussion

3.1 Thermal chemistry of azomethane

The adsorption of azomethane on Rh(111) was performed at 90 K. The following gaseous products were detected by TPD measurements: azomethane (58 u), H₂ (2 u), N₂ (14 u) and C₂N₂ (52 u) (Fig. 1). Trace signals were detected at 27 u in the range 250–500 K. These weak signals can probably be attributed to the formation of HCN. Attempts were made to identify CH₃, C₂H₅, C₂H₆ and CH₂NH₂ (31 u), but without any positive results. The same product distribution was observed by Bol et al. In our case, the detailed coverage-dependent TPD measurements reveal the following picture.

Azomethane desorbs from the surface in two peaks, one at 126 K and the other at 148 K. At very low exposure, there was no azomethane desorption, indicating that the parent molecule totally decomposes below 140 K. On increasing the exposure a TPD signal due to a chemisorbed layer appeared at 148 K. Even higher exposures led to the peak at 126 K becoming the dominant feature; it could not be saturated. This peak corresponds to multilayer sublimation. Monolayer coverage was defined as the maximum exposure (180 s), that was no multilayer peak. H₂ evolved in three well separated coverages.

3.1.1 Azomethane adsorption on Rh(111)

We observed no vibration at 2999–3008 cm⁻¹ which was a strong band characteristic of the trans-isomer at 2915 cm⁻¹. In this form the order of the CN bond is less than two. If it is a trans-form, can give IR bands in the range 1300–1400 cm⁻¹. In our case, the detailed coverage-dependent TPD measurements reveal the following picture.

Azomethane desorbs from the surface in two peaks, one at 126 K and the other at 148 K. At very low exposure, there was no azomethane desorption, indicating that the parent molecule totally decomposes below 140 K. On increasing the exposure a TPD signal due to a chemisorbed layer appeared at 148 K. Even higher exposures led to the peak at 126 K becoming the dominant feature; it could not be saturated. This peak corresponds to multilayer sublimation. Monolayer coverage was defined as the maximum exposure (180 s), that was no multilayer peak. H₂ evolved in three well separated coverages.

3.1.2 Azomethane decomposition

We observed no vibration at 2999–3008 cm⁻¹ which was a strong band characteristic of the trans-isomer at 2915 cm⁻¹. In this form the order of the CN bond is less than two. If it is a trans-form, can give IR bands in the range 1300–1400 cm⁻¹. In our case, the detailed coverage-dependent TPD measurements reveal the following picture.

Azomethane desorbs from the surface in two peaks, one at 126 K and the other at 148 K. At very low exposure, there was no azomethane desorption, indicating that the parent molecule totally decomposes below 140 K. On increasing the exposure a TPD signal due to a chemisorbed layer appeared at 148 K. Even higher exposures led to the peak at 126 K becoming the dominant feature; it could not be saturated. This peak corresponds to multilayer sublimation. Monolayer coverage was defined as the maximum exposure (180 s), that was no multilayer peak. H₂ evolved in three well separated coverages.

3.1.3 Azomethane dissociation

We observed no vibration at 2999–3008 cm⁻¹ which was a strong band characteristic of the trans-isomer at 2915 cm⁻¹. In this form the order of the CN bond is less than two. If it is a trans-form, can give IR bands in the range 1300–1400 cm⁻¹. In our case, the detailed coverage-dependent TPD measurements reveal the following picture.

Azomethane desorbs from the surface in two peaks, one at 126 K and the other at 148 K. At very low exposure, there was no azomethane desorption, indicating that the parent molecule totally decomposes below 140 K. On increasing the exposure a TPD signal due to a chemisorbed layer appeared at 148 K. Even higher exposures led to the peak at 126 K becoming the dominant feature; it could not be saturated. This peak corresponds to multilayer sublimation. Monolayer coverage was defined as the maximum exposure (180 s), that was no multilayer peak. H₂ evolved in three well separated coverages.

3.1.4 Azomethane recombination

We observed no vibration at 2999–3008 cm⁻¹ which was a strong band characteristic of the trans-isomer at 2915 cm⁻¹. In this form the order of the CN bond is less than two. If it is a trans-form, can give IR bands in the range 1300–1400 cm⁻¹. In our case, the detailed coverage-dependent TPD measurements reveal the following picture.

Azomethane desorbs from the surface in two peaks, one at 126 K and the other at 148 K. At very low exposure, there was no azomethane desorption, indicating that the parent molecule totally decomposes below 140 K. On increasing the exposure a TPD signal due to a chemisorbed layer appeared at 148 K. Even higher exposures led to the peak at 126 K becoming the dominant feature; it could not be saturated. This peak corresponds to multilayer sublimation. Monolayer coverage was defined as the maximum exposure (180 s), that was no multilayer peak. H₂ evolved in three well separated coverages.

3.1.5 Azomethane decomposition

We observed no vibration at 2999–3008 cm⁻¹ which was a strong band characteristic of the trans-isomer at 2915 cm⁻¹. In this form the order of the CN bond is less than two. If it is a trans-form, can give IR bands in the range 1300–1400 cm⁻¹. In our case, the detailed coverage-dependent TPD measurements reveal the following picture.

Azomethane desorbs from the surface in two peaks, one at 126 K and the other at 148 K. At very low exposure, there was no azomethane desorption, indicating that the parent molecule totally decomposes below 140 K. On increasing the exposure a TPD signal due to a chemisorbed layer appeared at 148 K. Even higher exposures led to the peak at 126 K becoming the dominant feature; it could not be saturated. This peak corresponds to multilayer sublimation. Monolayer coverage was defined as the maximum exposure (180 s), that was no multilayer peak. H₂ evolved in three well separated coverages.
Table 1  Frequencies (cm$^{-1}$) and assignments of the fundamentals of azomethane adsorbed on different transition metal surfaces, and solid azomethane

<table>
<thead>
<tr>
<th>Trans -solid</th>
<th>Cis -solid</th>
<th>Pt(111) mono</th>
<th>Mo(110) mono</th>
<th>Rh(111) mono</th>
<th>Rh(111) multilayer</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2975</td>
<td>3008</td>
<td>2999</td>
<td></td>
<td>2972</td>
<td>2976</td>
<td>v$_i$(C-H)</td>
</tr>
<tr>
<td>2966</td>
<td>2969</td>
<td></td>
<td></td>
<td>2962</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2971</td>
<td>2840</td>
<td></td>
<td></td>
<td>2915</td>
<td>2915</td>
<td>v$_i$(C-H)</td>
</tr>
<tr>
<td>2847</td>
<td>2882</td>
<td></td>
<td>2882</td>
<td>2951</td>
<td>2951</td>
<td>v(C-H)$_2$</td>
</tr>
<tr>
<td></td>
<td>2836</td>
<td></td>
<td>2836</td>
<td>2951</td>
<td>2951</td>
<td>v(C-H)$_2$</td>
</tr>
<tr>
<td></td>
<td>2752</td>
<td></td>
<td>2752</td>
<td>2951</td>
<td>2951</td>
<td>v(C-H)$_2$</td>
</tr>
<tr>
<td>1556</td>
<td>1540</td>
<td>1540</td>
<td>1570</td>
<td>1445</td>
<td>1445</td>
<td>v(N=N)</td>
</tr>
<tr>
<td>1545</td>
<td></td>
<td></td>
<td></td>
<td>1438</td>
<td>1438</td>
<td>v(C-N)</td>
</tr>
<tr>
<td>1450</td>
<td>1472</td>
<td>1415</td>
<td>1432</td>
<td>1381</td>
<td>1386</td>
<td>$\delta$(HCCN) and $\delta$(CH$_3$)</td>
</tr>
<tr>
<td>1443</td>
<td>1466</td>
<td></td>
<td></td>
<td>1386</td>
<td></td>
<td>$\delta$(HCCN) and $\delta$(CH$_3$)</td>
</tr>
<tr>
<td>1433</td>
<td>1437</td>
<td></td>
<td></td>
<td>1120</td>
<td></td>
<td>$\gamma$(C-N)</td>
</tr>
<tr>
<td>1386</td>
<td>1369</td>
<td>1315</td>
<td></td>
<td>1381</td>
<td>1386</td>
<td>$\delta$(HCCN) and $\delta$(CH$_3$)</td>
</tr>
<tr>
<td>1373</td>
<td>1361</td>
<td></td>
<td></td>
<td>1386</td>
<td></td>
<td>$\delta$(HCCN) and $\delta$(CH$_3$)</td>
</tr>
<tr>
<td>1330</td>
<td>1349</td>
<td></td>
<td></td>
<td>1180</td>
<td></td>
<td>$\gamma$(C-N)</td>
</tr>
<tr>
<td>1112</td>
<td>1178</td>
<td></td>
<td></td>
<td>1120</td>
<td></td>
<td>$\gamma$(C-N)</td>
</tr>
<tr>
<td>1001</td>
<td>1098</td>
<td>1010</td>
<td>1080</td>
<td>1007</td>
<td>1003</td>
<td>$\gamma$(C-N)</td>
</tr>
</tbody>
</table>

This table lists the frequencies and assignments of the fundamentals of azomethane adsorbed on different transition metal surfaces, and solid azomethane. The assignments are based on the vibrational spectroscopy of the adsorbed species.

3.2 Photo-induced chemistry of azomethane

This section deals with photon-driven chemistry, which occurs mainly in the first layer. The most informative TPD products at monolayer coverage as a function of irradiation time are displayed in Fig. 4. The thermal desorption characteristics of the parent molecule did not change in response to UV light, but the amount of azomethane slightly decreased with increasing irradiation time. At higher coverages of azomethane, the effect of UV illumination could be observed by following the molecular traces of the parent molecule at 38 and 43 u. The peaks characteristic of the desorption of azomethane from the monolayer disappeared and a new desorption feature developed at T$_{pe}$ = 135 K; this is attributed to a new desorption form with slightly altered chemical behaviour.

The appearance of a new species is also visible in the RAIRS spectra taken after UV irradiation (Fig. 5). At both monolayer and multilayer coverages new bands developed at 2930, 2878, 2854, 1720, 1471, 1350 and 1120 cm$^{-1}$ after a relatively long illumination time. The appearance of new peaks in the C-H-stretching (2950-2820 cm$^{-1}$) and the deformation (1300-1500 cm$^{-1}$) regions indicates some transformation in the terminal CH$_3$ groups. The band at 1120 cm$^{-1}$, assigned to $\gamma$(N-H)$_2$ clearly reflects the tautomerization of azomethane to formaldehyde methylhydrazine. A weak signal could also be detected at 1720 cm$^{-1}$, attributed to the $\gamma$(C-N) stretching vibration, but unfortunately the $\gamma$(N-H) and $\delta$(N-H) vibrations (characteristic features of the tautomer) could not be observed above 3300 cm$^{-1}$ and below 900 cm$^{-1}$ because of the low sensitivity of our spectrometer in these regions.

One of the most important effects of irradiation is the appearance of CH$_3$NH$_2$ in the TPD spectrum at 31 u at T$_{pe}$ =
124 K, with a high-temperature tailing. This feature was not observed in dark experiments; its intensity increased in response to UV photon exposure (Fig. 4A). The peak temperature of CH₃NH₂ (Tₚ = 124 K) is in good agreement with that found in a previous study of CH₃NF₁₂ adsorption on Rh(111) by Schmidt et al. The low temperature of CH₃NH₂ desorption indicates a desorption-limited process, i.e. the CH₃NH₂ molecule is produced by illumination or by direct decomposition of the tautomer on heating to 120 K. The presence of the IR band at 1471 cm⁻¹ could be assigned to δ(CH₃) of CH₃NH₂, and the other observed bands are also close to the fundamentals of CH₃NH₂ but the close similarity to those of azomethane makes it impossible to draw the conclusion that CH₃NH₂ is present at 90 K as an effect of illumination. The formation of CH₃NH₂ necessitates a lower temperature than 124 K (desorption of the molecule), as, without illumination, we could not detect CH₃NH₂ either adsorbed or in the gas phase. Above this temperature the dehydrogenation of the presumed intermediate (HN-CH₃) to NCH₂ is faster then the hydrogenation process, explaining the absence of CH₃NH₂ in the dark experiments.

C₂N₂, which was the main product in dark experiments, could not be observed even after a short irradiation time (Fig. 5). The extent of HCN formation, which was detected only in traces without irradiation, markedly increased in response to UV illumination. HCN desorption peaks were observed at Tₚ = 296, 354, 426 and 536 K. The N₂ and H₂ TPD features remained the same as those observed without irradiation; however, their amounts decreased slightly. The disappearance of C₂N₂ desorption can be explained by the reduced amount of CN groups. A large amount of azomethane is tautomerized to the hydrazone form and/or dissociates into CH₃NH₂; most of the latter desorbs without further dissociation to CN. At low coverages, CN groups decompose to C and N instead of undergoing recombination at elevated temperature.

The rather complicated structure of the desorption of HCN and H₂ is not yet completely understood, but should be controlled by the surface concentrations of H and CN-containing species and by the reactions between them.

The other significant effect of irradiation is the appearance of CH₄ in the desorption products, as can be seen in Fig. 4C. The amount of CH₄ increased with the illumination time, indicating a certain extent of C-N bond breaking as in the gas-phase photochemical mechanism of azomethane. The first step in CH₄ evolution is the formation of an adsorbed CH₃ group, and consequently the stretching vibration at 2920 cm⁻¹ increases in Fig. 5. In agreement with the former measurements, adsorbed CH₃ is self-hydrogenated into CH₄, which is desorbed at a peak temperature of 150 K. During irradiation, a small rise in the N₂ signal is observed isothermally, demonstrating photolytic decomposition at 90 K. Yates et al. found that only trans-azomethane produces CH₄ photolytically on Pd(111). As we could also detect CH₄ desorption after illumination of the first layer, this confirms the presence of the trans-form in the monolayer on Rh(111), which was not found either on Pd(111). Pt(111)² or Mo(110).³

Some changes as compared to dark experiments could be seen in the RAR spectra after annealing of the illuminated layer. There is a broader band near 1350 cm⁻¹, which is shifted to lower values and consists of two poorly resolved peaks. The FWHM of this feature becomes smaller above 265 K, and disappears by 300 K. The band at 1408 cm⁻¹ appears at much lower temperature (150 K) after illumination. It is the most intense feature in this region in the range 200–300 K, while the band at 1395 cm⁻¹ could not be detected above 255 K. In dark experiments, the above-mentioned peaks appeared and disappeared in reverse order, as can be seen in Fig. 3 (the dashed lines denote the illuminated sample). We can conclude from this observation that the thermal dissociation of the tautomer form is slightly different to that of the parent azomethane. The dissociation of the N-N bond in the tautomer forms HN-CH₃ and N=CH₂. The latter or its tautomer form (HN=CH₂) is probably responsible for the band at 1408 cm⁻¹, which appeared at much higher temperature (above 230 K) without UV irradiation. NH-CH₂ is partially dehydrogenated, presumably to (HN)CH₂, as indicated by the disappearance of the band at 1398 cm⁻¹ and the enhancement of that at 1408 cm⁻¹. Above 300 K, the fragment (HN)CH₂ is transformed to CNH₂, as in dark experiments. The only difference between the findings of illuminated and dark experi-
Acknowledgements

This work was supported by the Hungarian Academy of Sciences and OTKA grant T32040.

References