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Electron-induced modifications in thin solid films of nitromethane-D_3 with hydrocarbon admixture

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Abstract. The effect of electron exposure at an incident energy of 10.5 eV on solid molecular multilayer films containing nitromethane-D_3 has been studied by high-resolution electron-energy-loss (HREEL) spectroscopy. Nitromethane-D_3 was mixed with varying amounts of hexane or heptane to investigate whether the hydrocarbon component or, more specifically, resonant H^- production which is known to occur at electron energies around 10 eV plays a role in electron-induced modifications of the nitro group. While bands related to vibrations of the nitro group clearly diminish under exposure, the rate of this process does not depend on the amount of the admixed hydrocarbon component. Consequently, the hydrocarbon component and thus also the H^- producing resonance around 10 eV do not determine the rate of modification of nitromethane-D_3 at the investigated energy.

PACS. 68.49.Jk Electron scattering from surfaces – 61.80.Fe Electrons and positron radiation effects – 79.20.Uv Electron energy loss spectroscopy

1 Introduction

The potential application of ultrathin organic films and especially self-assembled monolayers (SAMs) as resist materials in low-energy electron lithography attracts considerable interest [1–5]. SAMs consisting of biphenylthiols attached to an Au surface have been shown to undergo crosslinking under exposure to 50 eV electrons and thus to act as negative resist [1]. This behaviour is also found for the same type of film functionalised with nitro groups but, in addition, evidence from XPS results suggests that the nitro groups undergo a chemical transformation to amino groups under the same conditions [2]. Similar results were obtained at an electron energy of 500 eV for SAMs on silanized silicon carrying 4-nitrobenzaldiimine [3], 4-nitrobenzamide [4], and related functionalities [3,5]. The selective chemical modification of the surface when irradiated through a mask provides anchor points for more complex surface modifications [2,4].

Although these results are highly interesting, the mechanism underlying the formation of the amino groups remains to be understood. It has been suggested that the hydrogen atoms required for the formation of amino groups are generated by the electron-induced dissociation of the C–H bonds in the hydrocarbon units of the SAM [2,3]. Electron-induced reactions in gaseous nitromethane at energies below 10 eV have been investigated recently [6]. On the other hand, this former study did not address the question concerning participation of hydrogen atoms, or possibly hydrogen anions produced by dissociative electron attachment (DEA) as monitored mass spectrometrically by electron-stimulated desorption (ESD) of anions [7] in the initial steps of the observed loss of nitro groups in the SAMs [2–5]. If this was the case, the reaction should be most rapid at incident electron energies (E_0) around 10 eV where ESD of H^- is very prominent. Furthermore, transformation of the nitro group should be accompanied by a significant loss of C–H bonds and the rate of loss of nitro groups should depend on the quantity of hydrocarbon material in the system under investigation.

In order to find evidence for or against participation of the hydrocarbon component in the initial steps of the electron-induced nitro to amino transformation, this work investigates the loss of nitro groups in a model system consisting of mixed thin solid films of hexane or heptane and nitromethane-D_3. Electron-induced reactions in these samples have been studied by use of high-resolution electron energy loss (HREEL) spectroscopy in the range of vibrational excitations at $E_0 = 10.5$ eV. Results on pure films of the single compounds are also included for reference. Comparison between pure film of nitromethane-D_3 and mixtures with hexane of varying nitromethane-D_3 concentration shows that the reaction rate does not increase when an increasing amount of C–H bonds is present in the material. Furthermore, as evidence from vibrational spectroscopy for the formation of N–H bonds is missing so far [2], the resulting HREEL spectra of the mixture are searched for direct evidence for the formation of amino

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groups. The deuterated compound nitromethane-D_3 was chosen for the study in order to possibly be able to differentiate between different sources of hydrogen if the characteristic amino stretching vibrations should be observable.

2 Experiment

The experiments were performed using a conventional HREEL spectrometer with cylindrical deflectors [8] incorporated in an ion pumped UHV system reaching a base pressure in the 10^{-11} Torr range. The set-up has been described in detail previously [9]. The combined resolution of the two energy selectors was set between 9 and 13 meV full width at half maximum of the elastic peak. A current of the order of a few tenths of a nanoampere as measured with a picoamperemeter was applied to the platinum substrate. The incident-electron energy (E_0) was calibrated within ±0.2 eV as described previously [9].

Nitromethane-D_3 was purchased from Aldrich at a stated purity of 99%, heptane and hexane were spectroscopic grade (Fluka). All compounds were used as received. Thin molecular films are initially prepared from the gas phase using a gas-handling manifold. Known amounts of gas, measured from the differential pressure drop in a calibrated volume, are leaked via a stainless steel capillary having an opening located just in front of a polycrystalline platinum substrate held between 32 K and 35 K by a closed-cycle He cryostat. Contaminations of the samples were not obvious as judged from the HREEL spectra. The thickness of the condensed nitromethane-D_3 films was estimated at 5–10 molecular layers from the amount of gas needed to deposit a monolayer assuming no change in sticking coefficient for the adlayers. The amount of gas required for the formation of a monolayer was simply deduced from a comparison with measurements on other molecules of similar size [10]. The thickness of a heptane or hexane film produced from a specific amount of gas is thus estimated to be approximately twice that of a film of nitromethane-D_3 produced from the same amount of gas. The thickness of a mixed film consisting of three parts of nitromethane-D_3 and one part of hexane (3:1) would therefore exceed the thickness of a film of pure nitromethane-D_3 by roughly 25%. The procedures applied previously to determine the monolayer coverage were described in detail in [11]. The film thickness chosen for the present experiments exceeds 50% of the mean free path of electrons within the film as verified by recording the thickness dependence of the vibrational spectra. At the chosen thickness the intensities within the vibrational spectra have reached their maximum value. This indicates that only the topmost layers of the films are effectively probed. Interactions with the underlying substrate, therefore, have a negligible effect on the results presented here.

Changes within the molecular films were monitored by continuously recording HREEL spectra within the range of the vibrational excitations. Any observable reaction in the course of such an exposure experiment thus takes place within the area of the surface probed by the spectrometer. All spectra were recorded at specular geometry, i.e. with the incident and detection angle adjusted at 60° with respect to the surface normal. The intensities and more specifically, the relative intensities of the vibrational bands varied only to a minor extent when the monochromator geometry was changed to an approximately 20° off-specular setting. Also, the intensity variation of elastic peak with the incident angle was only marginal compared to that on the bare substrate. The molecular films are thus assumed to be largely disordered already after deposition. Changes in the intensities during an exposure experiment can therefore not be ascribed to changes in the diffraction properties of the film [12,13].

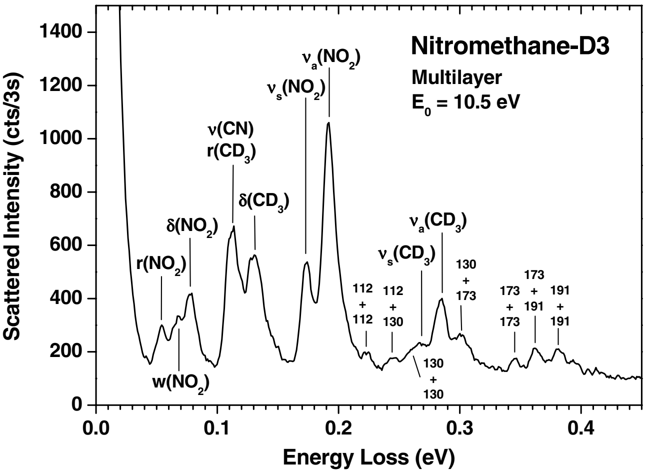


Fig. 1. Assignment of the bands within the vibrational HREEL spectrum of a multilayer film of nitromethane-D_3 recorded at $E_0 = 10.5$ eV. The spectrum has been recorded during approximately 40 min of electron exposure. Small numbers designate multiple scattering bands and their relation to the energy losses (meV) of the fundamental vibrational bands of nitromethane-D_3. The maximum of the elastic peak amounts to 15000 cts/3 s.

3 Results

The HREEL spectrum of a multilayer film of pure nitromethane-D_3 recorded at $E_0 = 10.5$ eV as applied throughout this study is shown in Figure 1. The assignment is given according to a previous ab-initio study on different partially deuterated nitromethanes [14]. Although not all vibrations can be resolved in the present HREEL spectrum, the relevant spectral ranges are clearly identified. In detail, the observed vibrations are the NO_2 rocking, wagging and deformation bands $r(NO_2)$, $w(NO_2)$, and $\delta(NO_2)$ at 55 meV, 68 meV, and 78 meV, an overlap of the CN stretching and CD_3 rocking bands $\nu(CN)$ and $r(CD_3)$ at 112 meV, the CD_3 deformation band $\delta(CD_3)$ at 130 meV, the symmetric and asymmetric NO_2 stretching bands $\nu_s(NO_2)$ and $\nu_a(NO_2)$ at 173 meV and 191 meV, as well as the symmetric and asymmetric CD_3 stretching bands $\nu_s(CD_3)$ and $\nu_a(CD_3)$ at 267 meV and 285 meV. In addition, smaller signals can be ascribed to multiple scattering bands resulting from electrons that

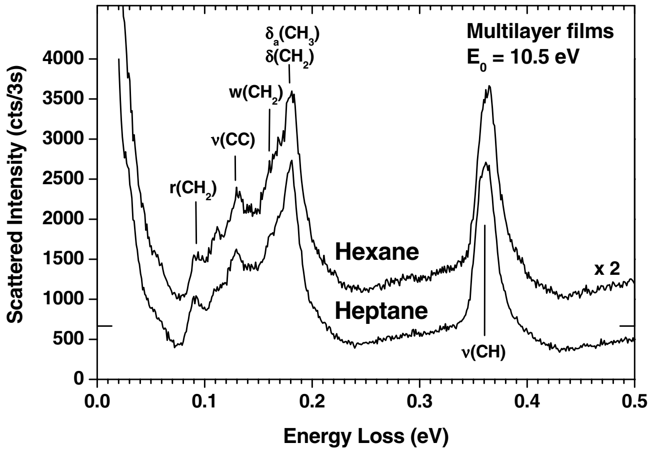
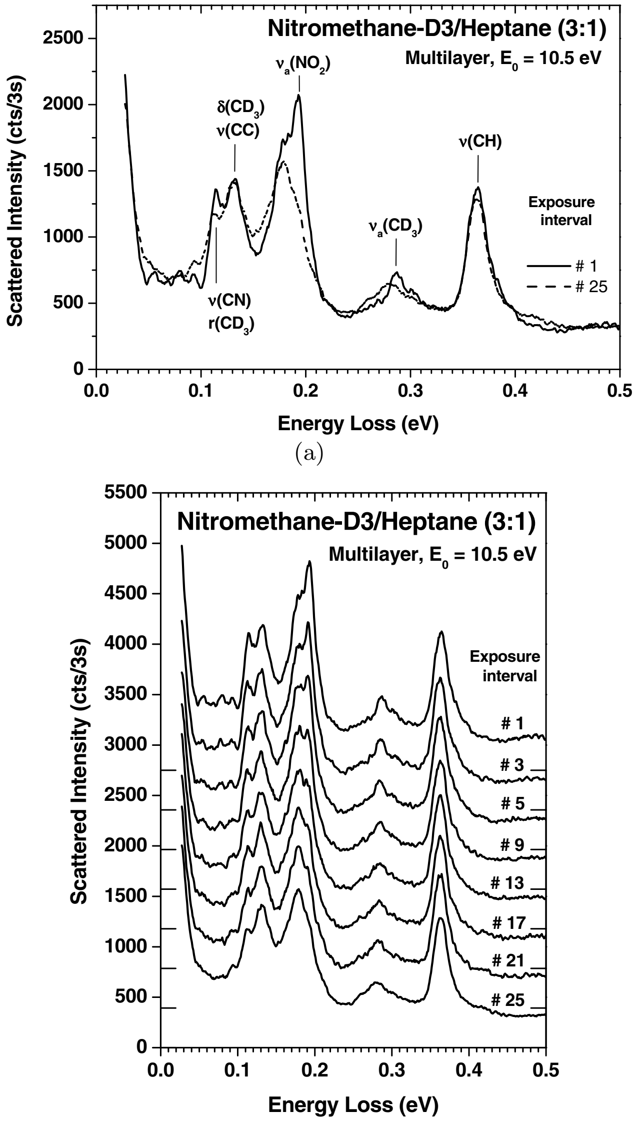


Fig. 2. Assignment of the bands within the vibrational HREEL spectrum of multilayer films of hexane and heptane recorded at $E_0 = 10.5$ eV. The spectrum of hexane has been recorded during approximately 30 min of electron exposure, the spectrum of heptane during 40 min. The spectrum of hexane is offset for clarity. The maximum of the elastic peak amounts to 26000 cts/3 s for hexane and 111600 cts/3 s for heptane.



(a)

(b)

Fig. 3. (a) Comparison of the HREEL spectra of a solid multilayer mixed film containing three parts of nitromethane-D_3 and one part of heptane (3:1) before and after prolonged exposure to electrons at $E_0 = 10.5$ eV. The maximum of the elastic peak amounts to 52900 cts/3 s for the first exposure interval. (b) Evolution of the same HREEL spectrum as a function of exposure time. Each exposure interval corresponds to approximately 40 min. Except for the last exposure interval all spectra are offset for clarity.

have undergone two subsequent inelastic scattering processes. Each of these bands is identified in Figure 1 by two numbers representing the energy losses in meV of the underlying fundamental excitations. Most importantly, most of the vibrations characteristic of the NO_2 groups are clearly separated from the deuterated alkyl signals within the spectrum of pure nitromethane-D_3. A change in the number density of nitro groups within the film should therefore be easily detected.

As reference, vibrational HREEL spectra of hexane and heptane are shown in Figure 2. The assignments included in the plot are not comprehensive and represent only some characteristic band positions as suggested by comparison with shorter-chain alkanes from reference [15]. Besides the CH stretching band located at 361 meV in heptane and 364 meV in hexane, the observed bands are most likely due to CH_3 and CH_2 deformation vibrations ($\delta_a(CH_3)$ and $\delta(CH_2)$) at 181 meV, an overlap of different wagging and deformation vibrations ($\delta_s(CH_3)$ and $w(CH_2)$) around 162 meV, a CC stretch ($\nu(CC)$) at 132 meV (hexane) or 130 meV (heptane), and a CH_2 rocking vibration ($r(CH_2)$) at 92 meV. An additional small signal at 112 meV can not be assigned with certainty but lies in the range of CH_3 rocking vibrations and additional CC stretching modes. As expected from the close relation of the chemical structures and the disordered film structure, the two spectra have a nearly identical habitus. Therefore, also the results of the exposure experiments described in the following and performed with either of the two compounds are closely comparable. The deviation in the absolute intensities between the two spectra shown in Figure 2 is probably an artifact of the spectrometer adjustment as the two measurements were performed at different times. On the contrary, each series of spectra that will be used to demonstrate modifications occurring within the samples under electron exposure, has been recorded within a short time without intermediate adjustment of the spectrometer. The intensity evolution in these cases of which a representative example is shown in Figure 3 is thus presented without any normalization of the data.

Exposure experiments were performed for both pure films of nitromethane-D_3 and mixed films of nitromethane-D_3 and heptane or hexane. In these experiments the films were continuously bombarded by electrons at $E_0 = 10.5$ eV. As a representative example,

Figure 3 shows the changes occurring in the vibrational spectra of a mixture of three parts of nitromethane-D_3 and and one part of heptane (3:1) during prolonged exposure to the electron beam at $E_0 = 10.5$ eV. After deposition of the film, a series of 25 spectra, each recorded during an approximately 40-min interval of electron exposure, has been acquired. For the sake of easier visualization, only selected exposure intervals showing the characteristic changes in the spectra are included in Figure 3. Figure 3a shows the overall changes in the spectra by superimposing data obtained during the first and last exposure interval. Bands related to the NO_2 groups that are identified in the mixture spectrum lose intensity under exposure (Figs. 3a and 3b). This applies mostly to $\nu_a(NO_2)$ at 191 meV, but also to the signal at 112 meV. Although overlapping with other signals from both the CD_3 group of nitromethane-D_3 and from heptane, this band coincides with the energy of the CN stretching mode (Fig. 1) so that its partial intensity decrease is consistent with a loss of C–N bonds. Furthermore, the bands $\delta(NO_2)$ at 78 meV and $r(NO_2)$ at 55 meV vanish although the intensity in this range increases, most probably due to overlap with new signals from unidentified reaction products. On the other hand, the intensities of the CH and CD stretching bands at 361 meV and 285 meV as well as the CD_3 deformation band $\delta(CD_3)$ at 130 meV which overlaps with the $\nu(CC)$ band of heptane remain roughly constant during exposure. The intensity evolution of $\nu(CH)$ will be discussed in more detail in Section 4.

To visualize the changes in nitromethane-D_3 more clearly, difference spectra were obtained by subtracting from the spectra of the mixture (Fig. 3b) for each exposure interval a fraction corresponding to 40% of the total intensity of the spectrum of pure heptane shown in Figure 2. This fraction has been adjusted until at a value of 0.4 a negative signal due to the CH stretching band at 361 meV just vanished. The subtracted fraction could be kept constant throughout the exposure series. The absolute value of this fraction is not significant as the absolute intensity delivered by the spectrometer may have changed slightly between the measurement of the heptane spectrum and the exposure experiment. Nonetheless, the fact that the same fraction could be used throughout the exposure experiment indicates that the heptane content does not vary noticeably under exposure. The result of the subtraction procedure is shown in Figure 4. Although the resolution suffers somewhat from the subtraction procedure, the spectrum during the first exposure interval is clearly that of pure nitromethane-D_3. With increasing exposure time, on the other hand, all bands related to vibrations of the nitro group clearly lose intensity while the $\delta(CD_3)$ and $\nu_a(CD_3)$ bands retain their intensity which for the latter band shifts towards the low-energy side. As intensity changes due to changing diffraction properties can largely be excluded because of the fact that the films are already strongly disordered prior to exposure, the observed intensity changes are traced back to a loss of nitro groups, i.e. an electron-induced reaction taking place within the film.

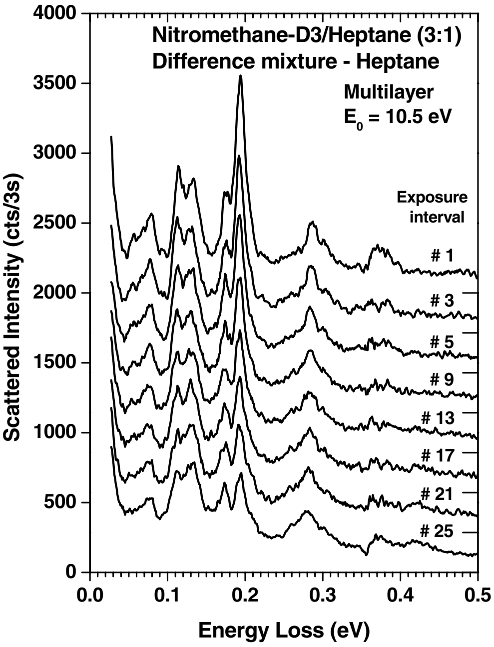


Fig. 4. Difference spectra obtained by subtracting from the spectra of the exposed mixed film of three parts of nitromethane-D_3 and one part of heptane (3:1) an amount of the spectrum of heptane (40% of the intensity in Fig. 2) that leads to an effective cancellation of the heptane ν(CH) band. Except for the last exposure interval all spectra are offset for clarity.

In order to investigate whether the hydrocarbon component of the film plays an important role in the loss of nitro groups, exposure experiments were performed for films containing varying amounts of the alkane component. The analysis of the results tries to correlate the rate at which the changes within the HREEL spectra occur to the amount of hydrocarbon material. A clear dependence of the reaction rate on the hydrocarbon concentration would demonstrate that reactive products of electron interaction with the hydrocarbon are intermediates in the sequence of reaction steps leading to loss of the nitro groups. In order to have comparable conditions, a series of such exposure experiments, this time consisting of subsequent 30-min spectra, has been performed within a short time without any adjustment of the spectrometer between the single experiments. The constant performance of the spectrometer during the whole series of experiments was obvious from very similar spectral intensities including the elastic peak recorded on the bare substrate prior to deposition of the samples. Pure nitromethane-D_3 as well as three different mixtures of nitromethane-D_3 and hexane were studied. Figure 5 shows the spectra of the mixtures during the first 30-min exposure interval in this series of experiments.

The determination of the reaction rates suffers from the fact that to some extent intensity fluctuations in the HREEL experiment may occur between the single spectra even if the spectrometer settings are retained. These intensity fluctuations can be the result of slight charging

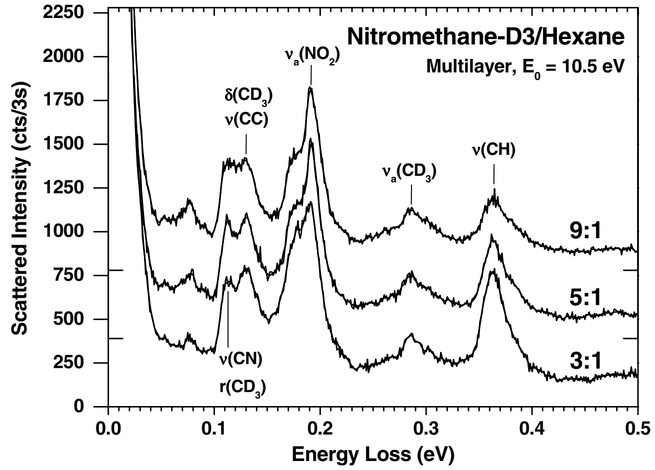


Fig. 5. Vibrational HREEL spectra during the first 30-min exposure interval for mixed films containing n parts of nitromethane-D$_3$ and 1 part of hexane (n:1) recorded at E_0 = 10.5 eV. The spectra of the mixtures (9:1) and (5:1) are offset for clarity. The maximum of the elastic peak amounts to 15300 cts/3 s for the (9:1) mixture, 16800 cts/3 s for the (5:1) mixture and 18300 cts/3 s for the (3:1) mixture.

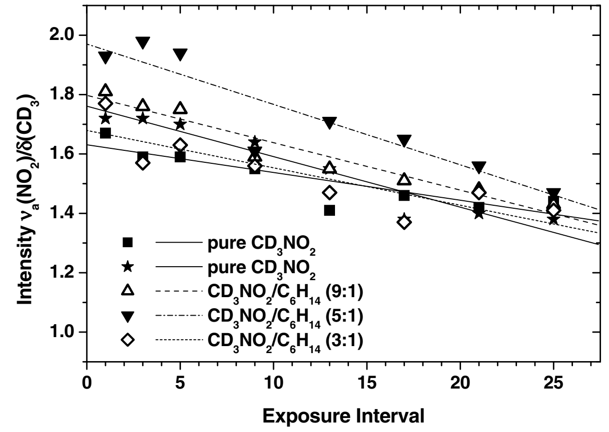


Fig. 6. Evolution of the intensity ratio $\nu_a(NO_2)/\ \delta(CD_3)$ in the HREEL spectra recorded at E_0 = 10.5 eV for solid multilayer pure films of nitromethane-D$_3$ and in difference spectra as a function of exposure time for selected exposure intervals. The difference spectra were obtained as shown in Figure 4 by subtracting from the spectra of mixed films of nitromethane-D$_3$ and hexane a specific amount of the spectrum of hexane from Figure 2. Each exposure interval corresponds to approximately 30 min. The lines represent a linear fit to each of the data sets.

effects of the sample or the spectrometer due to adsorption of gases at surfaces in the vicinity of the sample. These problems can be avoided by using in the analysis relative intensities, i.e. a ratio of two different but nearby bands, to monitor the progress of the reaction. The ratio of the intensities of the strongly varying $\nu_a(NO_2)$ band and the rather constant $\delta(CD_3)$ band was therefore chosen to visualize the changes in the reaction mixture under exposure. This ratio was obtained from the spectra of the mixtures after subtraction of an amount of the hexane spectrum that remained constant throughout each single exposure experiment analogous to the procedure used in Figure 4. Figure 6 shows this quantity as a function of exposure time for experiments on two different films of pure nitromethane-D$_3$ and the three different mixtures. The typical signal-to-noise ratio of the HREEL spectra as most obvious in Figure 2 limits the accuracy of the analysis especially in the subtraction step. This leads to a certain scatter in each of the data sets shown in Figure 6. Linear fits have thus been included as a guide to the eye. The margin of error of any deduced reaction rate is clearly demonstrated by the deviation in slope of the linear fit for the two exposure experiments on pure nitromethane-D$_3$. Nonetheless, within the accuracy of the experiment, all data fall within a similar range of values for the intensity ratio $\nu_a(NO_2)/\delta(CD_3)$ and slopes describing its change with time. More specifically, although the slopes and thus the reaction rates appear to vary somewhat from one experiment to the other, this variation does not correlate clearly with the concentration of the hydrocarbon material within the film. For example, the slope is somewhat larger for the (5:1) mixture than for both the (9:1) and the (3:1) mixture as well as one of the pure nitromethane-D$_3$ films. A dependence of the reaction rate on the hydrocarbon component can thus not be deduced. It must be noted that a drop of the intensity of the CH stretching vibrational band ν(CH) is observed during the first few exposure intervals (not shown). The drop observed in the third interval amounts to roughly 12% of the intensity during the first interval for the (9:1) mixture, 11% for the (5:1) mixture, 5% for the (3:1) mixture (Fig. 5), and 11% for the pure film of hexane (Fig. 2). Within the margin of error reflected by the lower value for the (3:1) mixture, loss of CH bonds thus does not clearly depend on the concentration of nitromethane-D$_3$ present in the sample. On the other hand, this conclusion must be regarded with caution as, in line with the above-mentioned intensity fluctuations, the intensity of ν(CH) increases after a longer exposure period, possibly due to effects of charging of the samples. Also, not only ν(CH) but also all other bands of both hexane and heptane drop during the initial stages of exposure. This behavior will be discussed below.

The question thus remains whether the observed changes in the HREEL spectra of both the pure films of nitromethane-D$_3$ and the mixtures in fact are related to a chemical modification or if they result from charging of the film. Such a charging would typically result from trapping of electrons within the organic film [16]. In that case, electrons impinging on the molecular film would be decelerated and hit the film at a lower E_0. As the changes within the film occur slowly, charging would also have to proceed gradually. An HREEL spectrum recorded at a certain time would thus reflect a certain amount of charge on the film. To verify if this effect could explain the observed spectral changes, HREEL spectra of a pure film of nitromethane-D$_3$ at low exposure were recorded for E_0 varying between 9.9 and 10.5 eV. All spectra (not shown) have the same habitus. Charging is therefore excluded as an explanation for the observed changes in the relative intensities of the nitromethane-D_3 spectra. In conclusion, the observed variations in the relative band intensities of nitromethane-D_3 under exposure to 10.5 eV-electrons must in fact reflect reactions occurring within the film.

4 Discussion

The central question addressed by this study concerns the reaction mechanism leading to loss of nitro groups in thin layers of organic nitrosubstituted materials. Three generally different reaction pathways may be formulated. (1) The reaction is initiated by electron-induced dissociation of CH bonds and the released neutral or anionic atomic hydrogen subsequently reacts with the nitro group. This mechanism has been proposed earlier [2,3]. (2) The reaction is initiated by electron-induced dissociation of NO bonds and the released neutral or anionic atomic oxygen subsequently attacks the hydrocarbon component of the film leading to hydrogen abstraction. (3) The dissociation of both CH and NO bonds is independent of each other and most of the reactive fragments either stay trapped within the film as such, recombine to form more stable species or escape to the vacuum.

Assuming that the drop of the relative intensity $\nu_a(NO_2)/\delta(CD_3)$ (Fig. 6) can be used as measure of the decay of nitromethane-D_3 or more specifically of loss of nitro groups, it is concluded that this decay does not depend on the amount of hydrocarbon present in the sample. Reaction mechanism (1) is therefore most probably not appropriate. Similarly, the apparent independence of the initial loss of CH intensity on the composition of the sample suggests that possibility (2) also must be excluded. In addition, it is interesting to compare estimated values for the consumption of hydrogen that would be expected if every oxygen atom that is lost in decay of the nitro groups reacted with the hydrocarbon component to form water in the extreme limit. In the experiments depicted in Figure 6, an average of 20% of the nitro groups has been consumed throughout the total exposure period. From the overall atomic composition and assuming water as the final product, the required loss of hydrogen or deuterium in the hydrocarbon component can be calculated. For example, in the (9:1) mixture, the atomic ratio O:D:H is 18:27:14. Loss of 22% of the nitro groups, as deduced from the exposure experiment, would lead to an added loss of 20% of CH and CD bonds and thus also of the intensity for the ν(CH) and ν(CD) bands. Similarly, for the (5:1) and (3:1) mixtures, nitro group losses of 26% and 20% would lead to CH/CD losses of 14% and 10%. In the pure nitromethane-D_3 sample, finally, the deduced loss of 20% of the nitro groups would infer the loss of 30% of the CD bonds if D_2O were formed. These values are clearly not reflected by the results from the exposure experiments where the overall intensity change of ν(CH) and ν(CD) is in most cases considerably smaller. It thus appears that at least a part of the fragments formed under exposure to electrons does not react to form stable end products, again yielding an argument against the predominance of reaction pathway (2).

Nonetheless, the somewhat confusing result that the CH stretching band drops during the initial stages of exposure to 10.5 eV-electrons to increase again later calls for a closer inspection of the effect. From the fact that the exposure experiments have been performed at an energy corresponding roughly to the maximum of the resonance leading to electron-induced dissociation of the C–H bonds in hydrocarbons as monitored mass spectrometrically by electron-stimulated desorption (ESD) of anions [7] some loss of hydrocarbon material must be expected. Absolute cross-sections for this process have been obtained from infrared measurements on alkanethiol-SAMs [17]. According to these results cross-sections for depletion of CH_3 groups vary from 1.2×10^{-16} cm^2 for octanethiol-SAMs to 5.3×10^{-16} cm^2 for hexadecanethiol-SAMs. With a typical incident current of 0.2 nA and an irradiated area of 1 mm^2, assuming that the thickness of the films in the present experiment is similar to that of the octanethiol-SAM, and that electron-induced CH dissociation is equally probable for all bonds, the CH signal could have dropped by roughly 7% during 1.5 h. This time corresponds approximately to the first three exposure intervals for the mixture and the hexane experiments. On the basis of this very crude estimate of incident current and irradiated area and neglecting the different nature of the samples, the amount of reaction deduced from the cross-section for the SAM films reflects the intensity changes of ν(CH) in the present exposure experiments reasonably well. It is unclear, however if the reported cross-sections [17] are also characteristic of the CH_2-units. If this was not the case, CH dissociation might proceed much more easily at the methyl groups and an apparent depletion cross-section representing an average over the different molecular CH sites might be considerably smaller in accord with the very low drop of the CH stretching signal under exposure. This interpretation would also be consistent with the finding that formation of C=C bonds with characteristic vibrational band close to 200 meV as reported previously in films of cyclopropane under exposure to electrons [10] is not clearly observed in Figures 3 and 4. Formation of such unsaturated hydrocarbon units would be the very likely consequence of CH bond dissociation in a hydrocarbon material.

Finally, when the intensity evolution of ν(CH) is discussed, its overlap with multiple scattering signals obvious from Figure 1 must be taken into account. Such bands must also decrease when some of the initial intensity in the range of the fundamental vibrations is lost. The multiple scattering bands within the range of ν(CH) are essentially double losses relating to fundamental bands in the 170 to 200 meV-range. Therefore, the decrease of these latter bands must also lead to a reduction of the multiple scattering intensity. From the relative intensities of multiple scattering and the fundamental bands in Figures 1 and 3 we can estimate that roughly 20% of the intensity in the ν(CH) range (Fig. 3) stems from multiple scattering bands during the first exposure interval. During exposure, the intensity in the 170 to 200 meV range changes by approximately 25% (Fig. 3b). The corresponding multiple scattering intensities which are proportional to the product of the corresponding fundamental intensities should therefore decrease by approximately 50%, i.e. roughly 10% of the original intensity in the ν(CH) range. This effect may therefore contribute to the observed initial change in intensity of ν(CH) (Fig. 3).

Apart from trying to solve the question whether the hydrocarbon component of an organic film plays a decisive role in the electron-induced modification of nitro-carrying molecules, this study also aims at direct spectroscopic evidence for the formation of amino groups under exposure to electrons. The previous study on SAMs of nitrobiphenylthiol on Au identified the formation of the amino groups after exposure to 50 eV-electrons from the N chemical shift in XPS spectra but did not record vibrational spectra within the range of the NH stretching vibrations [2]. For CD_3NH_2 and CH_3NH_2, the $\nu_s(NH_2)$ and $\nu_a(NH_2)$ bands are observed at 417 and 425 meV whereas the corresponding bands $\nu_s(ND_2)$ and $\nu_a(ND_2)$ in CD_3ND_2 appear at 307 and 317 meV [15]. Only very weak intensity in the former range is visible in Figure 3 after prolonged exposure. In other exposure experiments this signal is even less clear. Similarly, NH2 or ND2 deformation bands reported with high intensity at 201 meV and 152 meV in gas phase infrared spectra [15] are also not clearly identified here. Direct evidence for the formation of amino groups is therefore not provided by the present results. On the other hand, these bands could also not be detected in the HREEL spectra recorded at $E_0 = 6.5$ eV of an aminophenylthiol-SAM on Au and of samples of nitrobiphenylthiol-SAMs exposed to 50-eV electrons, i.e. treated under the same conditions that clearly produces amino groups according to the XPS results [18]. The NH stretching bands thus appear to carry little intensity in the HREEL spectra of amino substituted SAMs at least at $E_0 = 6.5$ eV. This effect remains to be investigated more closely.

Indirect evidence for the formation of amino groups from nitromethane-D_3 is possibly obtained from the range of the CD stretching vibrations. These bands are located more than 12 meV lower in gaseous CH_3NH_2 as compared to gaseous CH_3NO_2 [14,15]. The broadening of the CD_3 stretching band system upon exposure observed in Figure 3 may be attributed to this difference but this assignment also must be considered as tentative at this point.

5 Conclusions

The effect of exposure of thin solid films of nitromethane-D_3 and nitromethane-D_3 mixed with an alkane to electrons at an incident energy of 10.5 eV has been investigated in order to gain insight into the mechanism of electron-induced reactions of nitro-substituted molecular films. A loss of nitro groups under exposure is deduced from the decrease of the related vibrational bands. The rate of this reaction does not depend on the concentration of hydrocarbon material admixed to the nitromethane-D_3 film. In contrast to a previous suggestion [2,3], the hydrid producing resonant electron attachment process known to take place around $E_0 = 10$ eV thus does not play a rate determining role in the loss of nitro groups.

Another aim of this study was the search for direct evidence from vibrational spectroscopy that the nitro groups are reduced to amino groups under the effect of exposure to low-energy electrons. This direct proof can not be given as bands due to NH stretching and deformation vibrations could not be observed. This finding may hint towards a general insensitivity of HREEL spectroscopy in the solid phase to these signals but remains to be investigated more closely.

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