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UV photolysis in rare-gas solids: spectral overlap between absorbers and emitters

Leonid Khriachtchev^{*}, Mika Pettersson, Santtu Jolkkonen, Markku Räsänen

Laboratory of Physical Chemistry, University of Helsinki, P.O. Box 55, FIN-00014 Helsinki, Finland

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Abstract

The UV-photolysis kinetics of matrix-isolated species are discussed with respect to LIF measurements. The consideration is based on the concept of spectral overlap between light emitters and absorbers occurring during photolysis, and it develops further the model of self-limited photolysis proposed previously. We emphasise that these effects can strongly change the emission spectra and that evolution of the LIF signal during UV photolysis and annealing should be used with great caution in quantitative analysis of photochemical processes. On the other hand, the spectral overlap of narrow absorption bands with broad emission offers a spectroscopic approach to detecting the rising absorbers. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

UV photolysis is widely used in matrix-isolation research. The species studied are often unstable or difficult to directly deposit into a matrix, and in favorable cases they can be created in solid host by photolyzing a suitable precursor. After a photodecomposition event, the geminate photofragments can escape from the parent cage or they can be kept in the vicinity by the cage effect, hence forming either isolated fragments or complexes.

Laser-induced fluorescence (LIF) provides a sensitive approach to follow decomposing and appearing species if a characteristic emission can be excited

[1–3]. In particular, LIF allows one to study species isolated in a matrix in very small amounts including various IR-inactive species. LIF has repeatedly been employed to measure photolysis kinetics and changes introduced by the annealing of matrixes.

As a related example, H atoms in solid Xe can be probed by using the charge-transfer absorption in the 6.2–6.4 eV region and following the emission around 255 nm [4]. Surprisingly, it was noticed that the 255 nm emission of Xe_nH saturates much more quickly than the 193 nm photolysis of HBr in solid Xe, and some loss mechanisms for atomic hydrogen have been discussed [5,6]. As a result, a very long light-induced travel distance of H atoms in solid Xe (~10 nm) was extracted, and it was concluded that the maximum concentration of H atoms created during photolysis is more than an order of magnitude smaller than the maximum concentration of Br atoms. In

^{*} Corresponding author. Fax: +358-9-191-40279; e-mail: leonid.khriachtchev@helsinki.fi

contrast, the IR-absorption data for UV photolysis of HI and HCN in solid Xe indicate a much higher relative concentration of H atoms [7,8], which implies a significantly more limited flight distance of H atoms after cage exit. Moreover, the known molecular dynamics simulations of UV photolysis of related species in solid Xe do not predict very long travel distances either [3].

The disagreement between LIF and IR-absorption estimates on the concentration of H atoms in Xe matrixes can be understood by taking into account changes of optical properties during solid-state photolysis. By employing the model of optically thick matrices [9–11], we have recently demonstrated that matrix-isolation photolysis can be self-limited when the photofragments formed absorb the UV radiation [12]. Practically, this leads to a slowing down of the photolysis efficiency with time and to a saturation of the in-situ detected emission, and consequently the LIF signal does not follow the real product concentration. The effect has been demonstrated directly in the 193 nm photolysis of HCN/Kr matrices where the 775 nm emission of CN saturated faster than its IR absorption [12]. This experimental finding breaks the assumption of proportionality between the LIF signal and the product concentration made in Refs. [5,6] and disregards their numerical estimates for H-atom travel distance. Furthermore, it is highly possible that the consideration of corrupted LIF kinetics leads to an overestimate of dissociation efficiencies reported in the literature [13].

In this Letter, we consider further limitations on matrix-isolation LIF studies of UV-photolysis kinetics on the basis of the concept of spectral overlap between rising emitters and absorbers. We show that the overlapping absorbers can efficiently saturate the emission intensity during UV photolysis and strongly change the emission spectrum so that these effects should always be taken into account while analysing LIF modifications. We summarise the results of photochemical studies performed in our laboratory to clarify this statement. The present Letter does not contain a discussion of the various photolysis channels of the species used, and related details can be found elsewhere [8,14]. This Letter is partially motivated by the clearly contradictory literature estimates for the amounts of H atoms in photolyzed Xe matrixes [5–8,12].

2. Qualitative consideration

In order to describe LIF kinetics properly, a number of factors should be taken into account. First, rare-gas solids can often not be regarded as optically thin, and the depletion of the excitation field during its penetration into the matrix layer plays an important role in quantitative kinetic studies [9–11]. We emphasized the time evolution of this process in our model of self-limited photolysis [12]. In fact, if a matrix contains a sufficient number of precursor molecules, photogenerated new species can absorb the photolysis radiation and hence strongly decrease the photolysis efficiency for deeper layers of the sample. Moreover, in-situ-detected LIF of the photogenerated species appears to saturate faster than their averaged concentration. This effect has also been qualitatively discussed by Gödderz et al. [13].

The second factor influencing LIF kinetics concerns the photogenerated species which absorb at wavelengths of the emission in question. Indeed, the photolysis might simultaneously prepare a number of species, some of which absorb the emission from the others. If this absorption is strong enough, one can lose completely the desired emission because it simply does not escape from the matrix! In the more realistic case of a moderate absorber, it can still change the LIF intensity detected from different matrix depths. Because photolysis is not homogeneous, this process introduces an additional reason for differences between the LIF kinetics and the true concentration kinetics.

The third important factor to consider is Rayleigh scattering that changes the direction of light wave propagation due to optical inhomogeneity of the medium. Rayleigh scattering enhances the two effects mentioned above because it increases the path length of the radiation in the sample and limits penetration of the radiation into the deeper matrix layers even if the matrix absorption is rather weak. Rayleigh scattering alone destroys the ideal one-exponential photolysis kinetics for concentration due to the spatial redistribution of radiation intensity [12].

The LIF signal can be written in the general form

$$S(t, \lambda) \propto \int_0^L I(x, t) N(x, t) P(x, t, \lambda) dx, \quad (1)$$

where $N(x, t)$ is the concentration of emitters, $P(x, t, \lambda)$ gives the proportion of the emission reach-

ing the detector, and λ is the wavelength of the emission. In reality, it is quite impossible to derive analytical expressions for the three terms to be integrated because of the unknown inhomogeneous matrix morphology. Nevertheless, the qualitative outcome is clear. The deviation of $S(t)$ from $N(t)$ becomes important in scattering media and when the number of photogenerated absorbers is comparable with the available number of photons in one short laser pulse. In general, scattering and absorption of both photolysis and emission radiation limits the luminescence detection to the front matrix layer, and the LIF signal saturates faster than does the photolysis. In order to illustrate the last statement, let us consider the simplest numerical example that takes into account the absorption of LIF only: $I(x, t) = 1$, $N(x, t) = N(t)$, and $P(x, t) = \exp[-\alpha_0 N(t)x]$, where $\alpha_0 N(t)$ gives the absorption coefficient assuming that the amounts of the absorbers and emitters are equal. After integration of Eq. (1), we obtain

$$S(t) \propto (1 - \exp[-\alpha_0 N(t)L])cf/\alpha_0, \quad (2)$$

from which it can be seen that the signal is proportional to $N(t)$ for $\alpha_0 N(t)L \ll 1$, and it saturates for $\alpha_0 N(t)L > 1$.

It is important to consider explicitly the wavelength dependence of the effect. Without taking Rayleigh scattering into consideration, the detected emission spectrum is written in the form

$$S(\lambda) \propto I_0(\lambda) \int_0^L \exp[-x\alpha_L(x) - x\alpha_E(\lambda, x)] dx, \quad (3)$$

where $I_0(\lambda)$ is the true emission spectrum, α_L is the absorption coefficient at the photolysis wavelength, and α_E is the absorption coefficient at the emission wavelength. Thus, the detected emission spectrum can be corrupted depending on the $\alpha_E(\lambda)$ function.

As a qualitative conclusion of practical importance for matrix-isolation studies, the optical processes under consideration are of importance while extracting numerical dissociation parameters from LIF kinetics. The discrepancy between concentration and LIF kinetics curves can lead to an overestimate of light-induced travel distance and dissociation efficiencies. Furthermore, the damaged shape of emission spectra can result in misleading conclusions about the sites generated and can influence strongly

the analysis of FC factors for vibrational transitions. The effects become stronger for shorter photolysis/LIF wavelengths due to Rayleigh scattering, and they might be particularly problematic in vacuum-UV experiments.

3. Experimental results and discussion

The experiments were performed with rare-gas matrixes doped with various precursors that are mentioned specifically later. Typically, a matrix ratio of 1/2000, deposition temperature of 30 K for Xe and 20 K for Kr, and matrix thickness of 50 μm were used. A temperature of 7.5 K was kept during the photolysis and LIF studies. The samples were irradiated by various pulsed UV sources providing radiation with a pulse energy density of $\sim 5 \text{ mJ}/\text{cm}^2$ and pulse duration of 5–10 ns. Both FTIR and LIF spectra were measured in the same experiment. Further details of the matrix preparation, the experimental setup, and photolysis channels of the species under consideration can be found elsewhere [8,14].

During the 193 nm photolysis and annealing of the HCN/Xe matrixes, the HXe_n emission saturates much faster than the photolysis does, and this saturation has been explained in terms of self-limitation of the photolysis [12]. As well as saturation, the emission undergoes the spectral modifications illustrated in Fig. 1. In the beginning of the photolysis, the emission possesses a smooth shape, and it becomes structured after longer photolysis. Annealing at 45 K destroys the structure, and the emission after annealing corresponds to that in the early stages of photolysis.

As a second experimental example, Fig. 2a presents the emission from NO in solid Xe for two cases: (1) when NO is deposited from the gas phase and (2) when it is generated by the 193 nm photolysis of HNCO, which presumably involves the NCO–CNO isomerization and subsequent photodecomposition of CNO [14]. The upper spectrum is similar to the literature data [15,16] but the lower one, which displays NO obtained from HNCO, is very different because one emission band is practically absent. Furthermore, the emission from NO obtained from HNCO undergoes modification during the photolysis, and stabilizes the smooth shape after annealing at

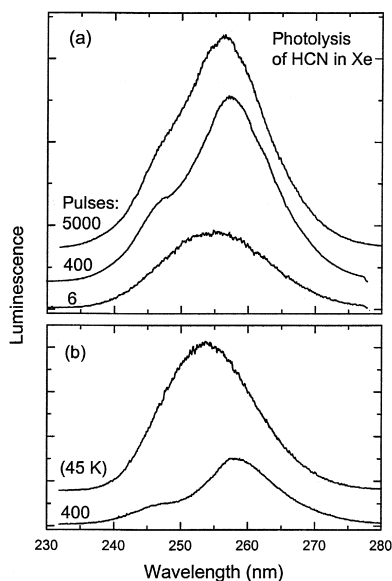


Fig. 1. The HXe_n emission measured (a) at different stages of the 193 nm photolysis and (b) before and after annealing of the photolyzed HCN/Xe matrix. The HXe_n emission is excited at 193 nm.

45 K. During the 193 nm photolysis of HNCO, the kinetics of NO emission and IR absorption are found to differ greatly from each other as demonstrated in Fig. 2b: the emission saturates after 180 pulses but the IR absorption band increases following further photolysis by a factor of ~ 5 .

Following the qualitative discussions of the previous section, the modification of the emission observed at different stages of UV photolysis and annealing of matrices can be explained by taking into account absorption of species whose concentrations change during photolysis and annealing. The absorption is wavelength-dependent, and this causes the observed modification of the emission. In other words, the emission in some spectral region is absorbed by a time-dependent species, and this process is described by the $P(x, t, \lambda)$ term in Eq. (1).

Indeed, we have no other reasonable explanation for the disappearance of one emission band in the NO progression generated in the 193 nm photolysis of HNCO/Xe matrices. For example, a site effect is incapable of producing such a modification. By using the model under consideration, the dramatic difference between the two curves in Fig. 2a is explained by absorption around 250 nm, which is small

in the as-deposited NO/Xe matrix but efficiently generated in the 193 nm photolysis of HNCO. A possible origin for this absorption will be discussed below.

This concept finds further support in the photolysis kinetics presented in Fig. 2b. In contrast to the IR absorption of NO, its emission measured at 265 nm saturates very quickly. An analysis shows that self-limited photolysis alone cannot describe numerically the behavior presented in Fig. 2b, and an additional saturating mechanism for the emission is required. It might be noted that the simplified model presented by Eq. (2) is capable of describing the experimental kinetic behavior by taking into account the absorption at 265 nm. Nevertheless, it is understood that the real photolysis is influenced by a number of additional processes and its kinetics is much more complicated.

In the beginning of the 193 nm photolysis of the HCN/Xe matrix, the HXe_n emission arises mainly

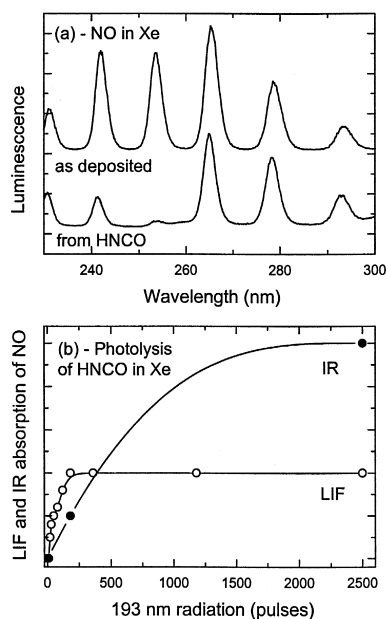


Fig. 2. NO in solid Xe. (a) The emission of NO as-deposited into the matrix (upper curve) and obtained in the 193 nm photolysis of HNCO (lower curve, 13000 pulses). (b) The kinetics of NO measured by LIF (open circles) and IR spectroscopy (solid circles) during the 193 nm photolysis of HNCO. The emission is excited at 225 nm and measured at 265 nm. The IR band at 1866.7 cm^{-1} is used to follow the NO concentration. The lines act as a guide to the eye.

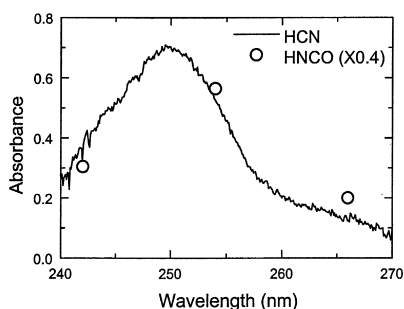


Fig. 3. The absorption rising in the 193 nm photolysis of HCN (line) and HNCO (circles) in solid Xe. The three data points obtained from the experiments with HNCO correspond to the three maxima of the NO emission.

from the front layer and absorption is not built up, which explains the unperturbed spectrum (see Fig. 1). During longer photolysis, matrix absorber(s) increase and the photolysis gradually penetrates into the bulk of the matrix, and the emission undergoes spectral perturbations. Annealing decreases the concentration of the absorber(s), and the emission approaches its unperturbed shape.

The model under discussion connects the changes of emission spectra with matrix absorption (see Eq. (3)). Qualitatively, this view is similar to the conventional scheme of UV absorption measurements where the emitter resembles a light source, and the only difference is the spatial overlap of the emitting and absorbing phases. It is seen that an averaged value of $\alpha_E(\lambda)$ can be extracted in a conventional manner for UV absorption spectroscopy if the emission spectrum is known. With regard to HXe_n , the true emission spectrum can be estimated roughly by using samples from an early stage of photolysis or annealed samples. For the unperturbed NO emission, we use the emission of as-deposited NO.

The result of the extraction procedure is presented in Fig. 3 for the 193 nm photolysis of the HCN/Xe (line) and HNCO/Xe matrices (circles). The extracted absorption spectra are similar for the two matrices although the absorption is much stronger for the photolyzed HNCO/Xe matrix. The rise of the absorption in photolysis and its decrease on annealing fully explain the modification of the emission spectra observed in our experiments.

It is difficult to identify the detected absorber at present, nevertheless, a tentative hypothesis can be

constructed. In order to get information about possible absorbers, we measured emissions of a number of photolyzed matrices excited at wavelengths in the 225–350 nm region. As a result, two distinct emissions were found, and they are shown in Fig. 4. The upper curve corresponds well to the known O–Xe charge-transfer emission [17], but the second emission has not yet been reported to our knowledge. The excitation profile for the known charge-transfer emission is measured to be around 240 nm, in good agreement with the literature data. The excitation profile of the second emission is red-shifted from the known O–Xe emission by ~ 30 nm. The lifetimes of the two emissions are practically identical (150 ns), and the emissions are of similar intensity. Both emissions are absent in as-deposited matrices, appearing during photolysis although their ratio changes at various stages of photolysis and annealing. Description of our extensive experiments with a number of precursors and photolysis wavelengths exceeds the scope of the present Letter. It is important to note only that we found *no examples* of one of the emissions arising in photolysis without the other one. These two emissions have been detected on photolysis of the following precursors in solid Xe: H_2O_2 , NO, HNCO, NO_2 , N_2O . Moreover, it seems that the blank Xe matrixes possessing only ordinary impurities such as water, oxygen and nitrogen give the two emissions under 193 nm photolysis as well. Of

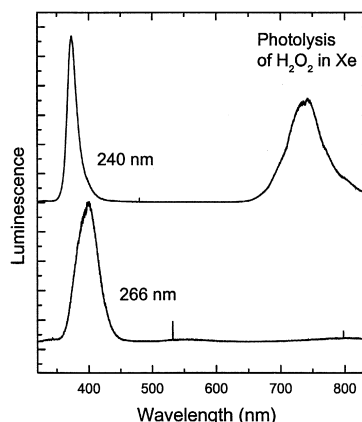


Fig. 4. Two emissions generated by UV photolysis of H_2O_2 in solid Xe. The emissions are excited at 240 and 266 nm as marked on the curves.

course, neither emission appears in Kr/Ar-matrix experiments.

We tentatively suggest that the emissions shown in Fig. 4 originate from atomic oxygen generated in the photolysis of oxygen-containing species. For example, the UV photolysis of $\text{H}_2\text{O}_2/\text{Xe}$ matrixes is known to give rise to free O atoms [18]. The two emissions might originate from two sites for O atoms in a Xe lattice as local coordination is capable of shifting charge-transfer states. We have no explanations why the second emission has not been reported in literature because it is very persistent and strong in our experiments. One possible reason is the different morphology of our disordered matrixes and the free-standing crystals used in Ref. [17]. Indeed, we have already demonstrated for closely related examples that the morphology influences emissions assigned to different sites [19], and the present study might offer one more example. The annealing experiments support the assignment of atomic oxygen as the absorber in question because the emission spectra normally stabilise their shape after annealing at 45 K, and this temperature is known to make O atoms mobile in solid Xe [20].

It should be noticed that excitation spectra of the two emissions do not fit exactly the absorption spectrum shown in Fig. 3, nevertheless, they overlap at the absorption maximum. Furthermore, photogenerated atomic oxygen might occupy other sites responsible for charge-transfer structures that contribute to the absorption around 250 nm but decay non-radiatively. We leave open the possibility of a different assignment for the absorption around 250 nm, although we have no other candidates for it.

4. Useful applications

The spectral overlap of matrix emission and absorption offers a convenient way to in-situ detect absorption bands without using conventional UV absorption technique. The essence of the approach is given by Eq. (3). This procedure does not possess generality but it might be useful in some particular cases. For example, the experimental arrangement can be unsuitable for conventional UV absorption measurements because of strong scattering and absorption by substrates or matrixes themselves. More-

over, our in situ approach might be useful for analysis with high spatial resolution (mapping), and it can be specifically surface-sensitive in contrast with integrated data of the conventional method. As a result, our approach is still applicable for strongly absorbing layers, in analogy with successful Raman spectroscopy of black samples. The generality of the present approach can be extended by fixing a suitable luminescent agent behind the matrix substrate or by doping matrixes with suitable emitters. In the following, we present two examples demonstrating the practical applicability of the proposed approach.

Our first example concerns 193 nm photolysis of HNCO/Xe matrixes. Before photolysis, 266 nm radiation excites a broad and weak emission around 340 nm, and the emission appears to come from the CsI substrate (see the dashed line in Fig. 5a). As a result of the 193 nm photolysis, a narrow hole at 338.5 nm appears in the substrate emission, indicating a rising absorber. Analysis of the literature shows

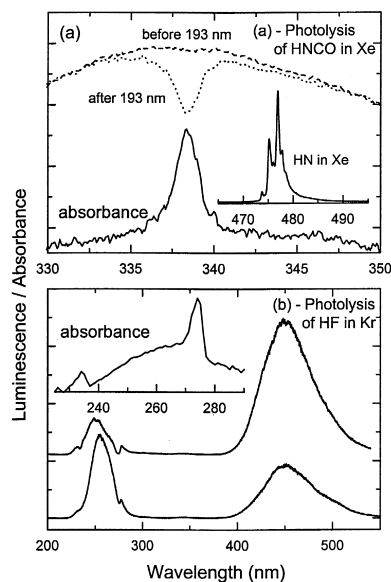


Fig. 5. Applications of spectral overlap between absorbers and emitters. (a) The CsI-substrate emission excited at 266 nm before (dashed line) and after (dots, 45 000 pulses) 193 nm photolysis of HNCO in solid Xe. The extracted absorption (solid line) originates from HN radicals. The HN emission excited at 338.5 nm is presented in the insert. (b) The emissions of HXe_2 and Kr_2F during in-situ 157 nm photolysis of HF in solid Kr, the two curves corresponding to different stages of photolysis. The extracted absorption spectrum of Kr_2F is presented in the insert.

that this absorption belongs to HN radicals [21], and the known HN emission is detected under the 338.5 nm excitation as demonstrated in the insert in Fig. 5a. The extracted HN absorption is presented by the lower curve. It should be emphasised that no IR absorption band of HN was detected in these photolysis experiments [14], which demonstrates the high sensitivity of the present method.

In order to expand the consideration to media different from solid Xe, we present the emissions observed in the 157 nm photolysis of HF/Kr matrixes (see Fig. 5b). The in-situ detected emission shows two broad bands: around 450 nm from Kr_2F [22,23] and around 255 nm most probably from HXe_2 in solid Kr [24], Xe being present in the matrix as an impurity. The sharp holes seen in the shorter-wavelength emission originates from the Kr_2F charge-transfer absorption. During photolysis, the F concentration increases, developing the absorption structure, which allows us to extract the absorption spectrum of Kr_2F . The extracted absorption spectrum is presented in the insert in Fig. 5b, and it is in good agreement with the Kr_2F excitation spectrum reported by Kunttu et al. [22]

5. Conclusions

We can formulate the following:

(1) Spectral overlap between emitters and absorbers rising in UV photolysis of matrix-isolated species changes the detected emission. The absorption of LIF further enhances the effects of self-limitation and Rayleigh scattering on LIF kinetics. We explicitly demonstrate these effects by presenting very different NO kinetics measured with IR absorption and LIF techniques. Thus, the kinetics of emission generated in photolysis should be used with great caution in quantitative analysis. If imperfection of matrix optics is not taken into account, the extracted light-induced travel distances and dissociation efficiencies can be strongly overestimated.

(2) The effect of rising absorbers can strongly modify the shape of emission detected from photolyzed matrixes, and this process probably explains the experimentally-observed modifications of the HXe_n and NO emissions in Xe matrixes. We tentatively suggest that the rising absorption is due to atomic oxygen at different sites. Analysis of matrix

sites and FC factors can be influenced by these spectral modifications.

(3) The spectral overlap of narrow absorption bands with broad emission offers useful spectroscopic approach to detect absorbers. The method is sensitive and practically applicable as demonstrated by the experiments with HNCO/Xe and HF/Kr matrixes.

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