

EXPERIMENTAL STUDIES ON PHOTODISSOCIATION OF HI IN CRYSTALLINE XENON

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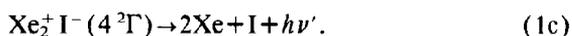
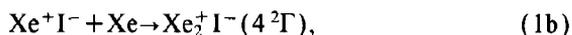
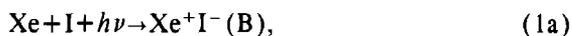
The photodissociation of HI at 277 nm in crystalline xenon is followed by monitoring the Xe₂I exciplexic emission. Above 110 K, the product I atoms diffuse and recombine as I₂. Between 110 and 80 K dissociation is permanent, and diffusion of I atoms is halted. Below 80 K amorphization of the solid is observed. The inclusion crystals are grown from the melt. Crystallinity is verified by the exciplexic lineshift.

1. Introduction

A theoretical study of the photodissociation of HI in crystalline xenon was recently presented [1]. These molecular dynamical simulations were inspired by the fact that such solids could be reproducibly prepared in our laboratory. The system can be regarded as one of the simplest prototypes of condensed-phase reactive dynamics, and as such may provide a fundamental understanding of many-body interactions. Three criteria are deemed essential for the successful execution of these studies, i.e. for a rigorous comparison between experiment and theory. These are: preparation of crystalline solids, verification of crystallinity, and a sensitive probe of dissociation products. The aim of this report is to communicate the satisfaction of all three criteria; and to report our preliminary observations, namely, a very strong temperature dependence in the permanent dissociation probability of HI.

In the present studies, a single radiation source is used for both dissociation of HI and detection of I atoms. The detection technique is based on inducing a charge transfer from xenon to iodine atoms and monitoring the Xe₂⁺I⁻ emission. The sensitivity of this technique for detecting halogen atoms in solid xenon has previously been discussed [2,3]. The pro-

cess, which forms the basis of the four-level laser analogy [4], can be summarized as:



The charge transfer absorption of (1a) is intense and peaks near 280 nm [3]. The reactive quenching in (1b) proceeds on a subpicosecond timescale in solid xenon such that no emission is observed from the diatomic exciplex. Therefore the triatomic exciplex is formed with near unity quantum yield. The relaxation of the triatomic in (1c) is strictly radiative in solid rare gases. Thus the emission intensity of the triatomic exciplex, upon 280 nm irradiation, is directly proportional to the I atom concentration. This excitation wavelength also coincides with the ³Σ₀ → ³Π₁ dissociative absorption of HI [5,6]. Therefore, a single radiation source is sufficient for both dissociation of the molecule, and detection of products. This experimental convenience is attained at the cost of complicating the interpretation of results. Since the absorption cross section of the charge transfer transition in (1a) can be estimated to be nearly two orders of magnitude larger than that of the HI absorption at 277 nm (see section 3); the effective radiation intensity reaching the HI molecules is severely attenuated during the course of irradiation. Thus, in order to obtain absolute rates of dis-

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sociation, the knowledge of accurate cross sections and careful account of the experimental geometry are required. Since such information is not available at present, only a qualitative assessment of the solid state photodynamics will be presented.

Finally, due to the ionic-neutral nature of the monitored exciplexic emission in (1c), and the large dipole of the exciplexic state, the emission band center is sensitive to its environment. The ionic excited state is solvated by dipole-induced-dipole interactions with the polarizable xenon atoms. Due to the R^{-6} dependence of this interaction, the shift is particularly effected by nearest neighbors, hence sensitive to the structure of the immediate solvent cage. This consideration holds the key to identification of the crystallinity of the sample, as demonstrated previously in studies of ICl in solid xenon [7].

2. Experimental

The experimental details have been previously discussed [7]. A high-pressure, three-window cryocell, cooled with a closed-cycle helium refrigerator is used. The crystalline samples are formed by slow cooling of the solution, 10–16 h, with stable temperature control (± 0.1 K). The transparent solids grow along a temperature gradient established by heating the gold-coated copper cell at opposite ends from the cold tip. By recording IR spectra in the liquid and solid phase, it was verified that no zone refining occurs in the case of HI/Xe solutions at concentrations as high as 25 mM. Therefore the guest to host ratio in the solid can safely be assumed to be the same as that of the solution.

Xenon of 99.999% stated purity was purchased and used without further purification. HI was distilled into a blackened glass bulb coated with halocarbon wax. In order to avoid contamination with I_2 , the bulb was cooled in an ice-water bath prior to transfer of the HI to the cryocell. HI is transferred to the cell at 200 K, sufficient xenon is immediately added to fill the entire cell with liquid. The reported experiments are from a 5.7 mM sample, an HI: Xe ratio of $\approx 1:5000$ in the solid. The solid is grown to fill the entire cell – a cylinder of 1.25 cm diameter and 4 cm length.

The doubled output of an excimer-pumped dye

laser (Lambda Physik EMG 201/MSC, FL3002) was used as excitation source. The output of the laser is soft-focused on the sample with a 1 m lens. Typical irradiation fluences were 6 mJ/cm^2 , at a repetition rate of 8 Hz. Emission at 90° from the excitation beam is collected with $f/4$ optics. The emission was dispersed through a 0.25 m polychromator and detected with an intensified diode array of 990 active elements. The output of diodes in a 20 nm spectral range (380–400 nm), corresponding to the $Xc_2^+ I^-$ emission band center, are summed and stored as a function of irradiation time.

3. Results and discussion

Emission spectra of Xe_2I in liquid (at 175 K) and solid (at 28 K) xenon are shown in fig. 1. The spectra are characteristically broad due to the bound-to-repulsive nature of the emission. In the liquid phase, beside the main emission a much weaker band can be seen near 560 nm. This is characteristic of all triatomic exciplexes observed in matrices [2,3] or solutions [8] of xenon. Three repulsive surfaces arise from the covalent interactions of two xenon atoms and a halogen atom [9]. Transitions to all three are allowed from the lowest ionic state, the $4^2\Gamma$ state. However, only two emissions can usually be identified [2]. The main band is assigned to unresolved emission terminating in the two lowest covalent repulsive surfaces $4^2\Gamma \rightarrow 1,2^2\Gamma$, while the red-shifted band is assigned to $4^2\Gamma \rightarrow 3^2\Gamma$. The solid-state spectrum in fig. 1 is substantially narrower than, and significantly blue-shifted relative to, the liquid-phase spectrum shown in the same figure. In addition, a weak red shoulder – that we assign to $4^2\Gamma \rightarrow 2^2\Gamma$ – becomes apparent on the main emission band, which is assigned to $4^2\Gamma \rightarrow 1^2\Gamma$. In matrix-isolated spectra of the triatomic rare gas halides, the transitions to $1^2\Gamma$ and $2^2\Gamma$ are usually inseparable, presumably due to inhomogeneous contributions effected by the amorphous nature of matrices. The narrowing of the $4^2\Gamma \rightarrow 1^2\Gamma$ emission and separation of the emission to all three ground states in the present case is an indication of the crystallinity of the environment and the absence of significant inhomogeneous contributions. The narrowing of the emission bands in the range of 160–25 K, which is observed both in the

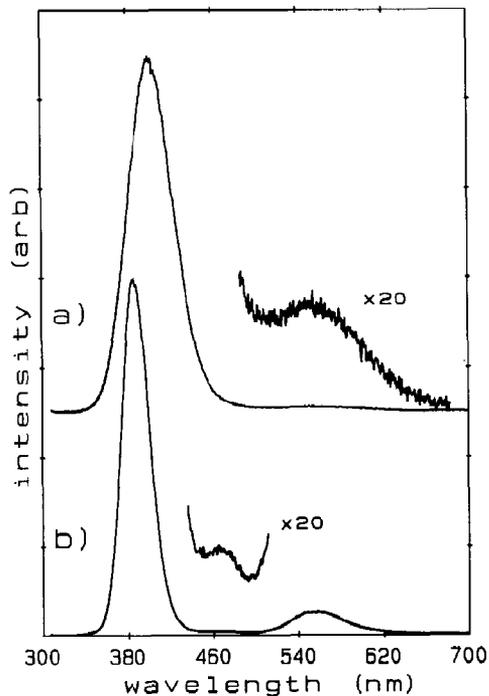


Fig. 1. Condensed-phase emission spectra of $\text{Xe}_2^+ \text{I}^-$ recorded from a sample of 1:5000 HI:Xe. (a) Liquid-phase spectrum recorded at 175 K, excitation fluence of 65 mJ/cm^2 at 267 nm. Two bands are observed: the main band, with a maximum at 400 nm, is assigned to unresolved $4^2\Gamma \rightarrow 1,2^2\Gamma$ emission; the weaker band (expanded scale) is assigned to $4^2\Gamma \rightarrow 3^2\Gamma$. (b) Emission spectra from crystalline xenon at 28 K, excitation fluence of 6 mJ/cm^2 at 277 nm. The main band with a maximum at 388 nm shows a shoulder (expanded scale) which is assigned to $4^2\Gamma \rightarrow 2^2\Gamma$.

main peak and the red-most emission, is attributed to the reduction in the vibrational temperature of the ionic state. The potential along the bending coordinate of the halogen ion relative to the Rg_2^+ axis is known to be very soft in triatomic rare gas halides [10].

The maxima of the main emission band of $\text{Xe}_2^+ \text{I}^-$ is plotted in fig. 2 as a function of temperature. In the liquid phase, a red-shift is observed as the temperature is lowered. Upon formation of the crystalline samples, an abrupt blue-shift is observed, which is absent in supercooled solids. This dramatic blue-shift upon phase transition is taken as an indication of the establishment of crystalline order. The arguments were previously presented in the case of studies in ICl [7]. Succinctly stated, in the exci-

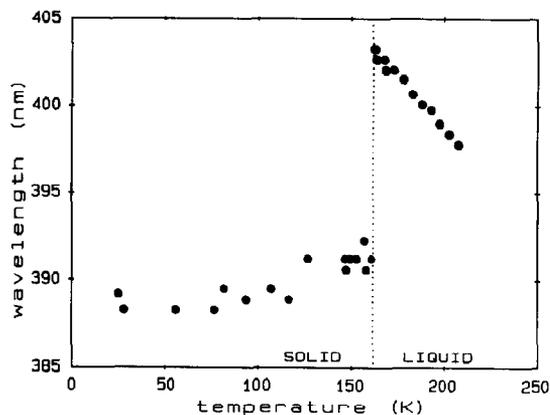


Fig. 2. Band maxima of $\text{Xe}_2^+ \text{I}^-$ main emission in condensed xenon as a function of temperature. The dotted line is drawn at the melting point of xenon (161.25 K). The band maxima undergo an abrupt shift upon phase transition.

plexic state the charge transfer is nearly complete, therefore the dipole of the emitting state is $\approx 10 \text{ D}$, and extensive clustering of the $4^2\Gamma$ state with the polarizable solvent atoms is to be expected in the liquid phase. If long-range order is established upon solidification, then clustering, i.e. collapse of the host cage around the exciplex, would be prevented due to the cohesive energy of the crystal which forces the host atoms to assume their respective lattice sites. Thus, the abrupt blue-shift that accompanies the phase transition in fig. 2 is taken as an indication of the dilation of the immediate cage, and therefore the establishment of long-range order.

Photodissociation studies were conducted as a function of temperature in the solid from which the spectroscopic results of figs. 1 and 2 were obtained. The temperature was lowered slowly in order to prevent strains and to provide annealing. The experiments were conducted during the cool-down cycle, over a period of several days. The exciplex emission was monitored as a function of irradiation time. As discussed in section 1, the total emission intensity is proportional to the I atom concentration in the volume of interrogation, and therefore proportional to *permanently* dissociated HI molecules. The experimental geometry dictated by the T-cell is such that the first $\approx 1 \text{ cm}$ of the irradiated volume is blocked from the view of the detector. Thus, the laser intensity reaching the observation volume is strongly attenuated by the charge transfer absorption of the

photogenerated I atoms. The severity of this consideration can be gauged from a comparison of the reagent and product absorption cross sections. At 280 nm, the HI absorption cross section is $8 \times 10^{-20} \text{ cm}^2$ in the gas phase [11]. The oscillator strength, f , of the charge transfer transition of eq. (1a) can be estimated from the known gas-phase radiative lifetime [12] of the XeI(B) state – 12 ns, centered at 253 nm – to be ≈ 0.08 . The absorption cross section can then be estimated from the excitation spectra of I-doped solid xenon [3] – excitation centered at 280 nm, with a width of $\approx 40 \text{ nm}$ – to be $\approx 1 \times 10^{-17} \text{ cm}^2$. While this estimate is approximate, it clearly indicates that attenuation of the probe beam by the product atoms will dominate the time evolution of the detected emission intensity. The results should then be interpreted with caution. In the studied temperature range, three different types of behavior are observed. These are illustrated in the three panels of fig. 3 and discussed below.

The high-temperature behavior, $160 < T \lesssim 110 \text{ K}$, is exemplified in the top panel of fig. 3. The basic features, namely the development of a maximum in the exciplexic emission and subsequent decay of the emission, were observed in measurements performed at 151, 146, 136, 126, and 116 K. As the temperature is lowered, both the growth and decay rate of the emission intensity are reduced. The two traces shown in the panel, recorded at 136 and 116 K, illustrate this behavior. Note that in each case the beam was moved to irradiate a fresh spot on the solid. The rapid rise in the I atom concentration implies an efficient photodissociation of HI. The subsequent fall is due to both reduction in the penetration depth of the excitation beam and due to the diffusion of I atoms out of the interrogation volume. Both of these effects could be verified visually. The diffusion of I atoms is verified by the observation of a yellow-brown coloration in the solid due to formation of I_2 . Thermal diffusion of I, or xenon atoms, is to be expected in these soft solids on the observation timescale of many seconds. Additionally, kinetic energy is imparted to the atoms both during the photodissociation of HI and in the radiative dissociation of the $\text{Xe}_2^+ \text{I}^-$ exciplex, promoting local melting and impulsive diffusion. While absolute dissociation probabilities and diffusion rates are not extracted due to the complications discussed above, it should be clear

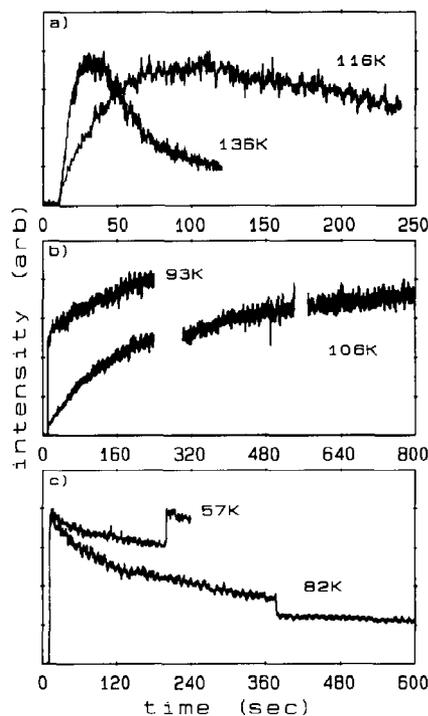


Fig. 3. Time evolution of I atom concentration followed by monitoring $\text{Xe}_2^+ \text{I}^-$ emission as a function of irradiation time. The data are from a 1:5000 HI:Xe crystalline solid, irradiated at 277 nm at 8 Hz and 6 mJ cm^{-2} per pulse, recorded at the indicated temperatures. (a) High-temperature behavior. The I atom concentration grows and decays with time in the volume of interrogation. Curves obtained by irradiating fresh spots have been normalized to the same height. (b) Intermediate-temperature behavior. Permanent dissociation and absence of decay are observed. The two curves were obtained by irradiating the same spot. The 93 K data was obtained 2 h after the 106 K data. The two curves are plotted on the same absolute scale. (c) Low-temperature behavior. The decay is due to amorphization of the solid. The data are obtained from previously irradiated regions. The catastrophic decays are exemplified by the sudden drop and the sudden increase in emission recorded at 82 and 57 K, respectively.

from the relative rates of growth and decay that both processes have a very strong temperature dependence.

The intermediate temperature behavior is exemplified by the middle panel in fig. 3. The two traces were recorded at 106 and 93 K, with a time lapse of 2 h between records. In this range of temperatures, between 110 and 80 K, the exciplexic emission grows slowly with time and reaches a plateau. As in the high-temperature range, the rate of growth is reduced as the temperature is lowered. The obvious implica-

tions are that HI is permanently dissociated, the permanent dissociation probability is subject to a strong temperature-dependent cage effect, and the product I atoms do not diffuse out of the interrogation volume. To verify the latter conclusion, after 15 min of constant irradiation at 106 K, the system was kept in the dark for 5 min and irradiation resumed. The emission intensity after the dark period continues at the same level as before, and remains constant at the plateau for another 15 min of irradiation: diffusion of neither I atoms nor recombination of H with I are significant at these temperatures on the timescale of 5 min.

The low-temperature behavior, $T < 80$ K, is exemplified by the lower panel in fig. 3. The exciplexic emission decays slowly with irradiation time and shows catastrophic behavior: sudden increase or decrease. Examples of each are shown in the traces of the panel. Along with the decay in emission, the solid becomes highly scattering and the penetration depth of the excitation beam is greatly reduced – amorphization of the crystal is clearly visible. It is interesting to note, however, that substantial healing of the crystal is observed when the system is kept at a constant temperature overnight. We can surmise that the crystalline solid cannot accommodate the energy released during the dissociation: an effect recently observed in molecular dynamical simulations of the same system [13].

4. Conclusions

The main points that we wish to communicate with this report are: (a) crystalline HI/Xe samples can be reproducibly prepared; (b) crystallinity of the samples can be conveniently verified by the dramatic phase transition observed in the exciplexic emission lineshift; (c) photodissociation dynamics in these solids can be studied with high sensitivity by interrogation of the charge transfer transitions of rare gas halides.

While we refrain from a quantitative analysis of the experimental observations, several qualitative

conclusions can be drawn. The permanent dissociation probability of HI in crystalline xenon is subject to a large, temperature-dependent, cage effect. This effect is undoubtedly due to the combination of cage exit and return probabilities [1]. Significant diffusion of product I atoms is observed at high temperatures. The diffusion rate decreases as the temperature is lowered such that below 110 K it is eliminated for all practical purposes. Destruction of the crystalline lattice is observed below 80 K, it is not clear whether this is a local or a bulk effect. Concentration and power dependence studies could resolve this issue.

These reported preliminary results are qualitative. Detailed studies, in which the detection technique is complemented by transient absorption is presently being implemented to derive absolute cross sections for dissociation, recombination, and diffusion at which point a direct comparison with theoretical simulations will be warranted.

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