

Observation of the Xe–S charge transfer emission in crystal Xe doped with OCS

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Abstract

In free standing crystals of Xe, OCS readily dissociates upon irradiation at 248 nm. On continuation of the laser irradiation, a broad emission centered at 346 nm was found to grow, which is assigned to the Xe–S charge transfer exciplex transition in the crystal. The temperature-induced mobility of S atoms is documented: upon warm-up, the intensity of the exciplex emission decreases with concomitant increase of the S₂(B → X) emission band intensity.

1. Introduction

In contrast with the rare gas oxides, the rare gas sulfide potentials are poorly known, and there is little information about their charge transfer states. Xu et al. have reported gas phase emission spectra of Xe⁺S⁻, generated by the reaction of Xe metastable with OCS [1]. They observed a broad emission centered at 227 nm, typical of bound-to-free transitions, which they assigned to the triplet charge transfer state. The absence of the expected singlet emission in the gas phase was attributed to its possible predissociation via a crossing with XeS (2 ¹Σ⁺), which asymptotically correlates with Xe + S(¹S). The same considerations also hold for the observed Xe⁺O⁻ emission [10]. The spectroscopy of S(¹S) in Ar and Kr matrices was most recently described by Zoval and Apkarian [2]. This state can be directly reached via S(¹S) → S(³P) excitation, and it relaxes by radiation on the S(¹S) → S(¹D) transition. Emission spectra from S(¹S), produced as a direct VUV photodis-

sociation product of OCS in various rare gas matrices, were presented by Taylor et al. [3,4]. In Xe the S(¹S) → S(¹D) occurs at ≈ 800 nm, red-shifted from its gas phase value of 772 nm. The ionic states of S in rare gas solids are not well documented, even though some evidence for their participation in the photodissociation of SH-doped Kr has been given [2]. Here, we present the first report of an emission band in S-doped solid Xe which can be ascribed to a charge transfer state between S and solid Xe. This emission can be used to monitor the photodissociation of OCS.

2. Experimental

OCS-doped free standing crystals of Xe were prepared in a closed-cycle cryostat equipped with four optical windows. The details of the growth scheme have been described previously [5]. The dilution ratio of the sample was varied from 1 : 1000

to 1:100000. The data to be reported, spectra and lifetimes, were independent of concentration. OCS was obtained from Matheson Co. and Xe of 99.99% stated purity, was purchased from Takachiho Shoji Co. Both gases were used without further purification. Irradiation of the crystals were carried out at ≈ 17 K, with a KrF laser (Lambda Physik 53 SMSC). The parallel laser beam was introduced through an iris of 2 mm \varnothing into the crystal without focusing, at a typical fluence of $0.5\text{--}5$ mJ cm $^{-2}$ pulse $^{-1}$. The repetition rate was 10 Hz.

Emission from the crystal was collected with quartz lenses ($d = 5$ cm, $f = 10$ cm), dispersed with a 0.25 m monochromator, and detected with a photomultiplier (Hamamatsu Photonics, R928). A boxcar integrator (EG&G model 4121B) was used for data acquisition and a personal computer was used for transfer and analysis of the data.

3. Results and discussion

When a pure Xe crystal was irradiated with a KrF laser (248 nm), weak emissions centered at 375 and 750 nm were observed, which were assignable to XeO charge transfer emissions [6]. The precursor of O atoms is probably contaminating O $_2$, but the intensity was weak, and we believe the effect of the contamination does not affect the following experimental observations.

A broad structureless emission band centered at 346 nm was observed to grow upon irradiation of OCS-doped Xe crystals with a KrF laser at 17 K. The observed spectrum, recorded with a spectral resolution of 0.2 nm, is shown in Fig. 1a. The emission decayed single-exponentially with a lifetime of 180 ± 10 ns, as shown in Fig. 2. Although much weaker, a well-resolved vibrational sequence in the spectra range between 370–460 nm was also observed when the crystal temperature was slightly higher. The latter emission increased when the crystal temperature was cycled up to 40 K and back to 17 K (Fig. 1b). The structured emission can be identified as the S $_2$ (B–X) transition, which has been well documented in prior studies in matrices [7,8]. S $_2$ can absorb the 248 nm light to yield the vibrationally excited B state [9].

When CS $_2$ or H $_2$ S was employed in place of

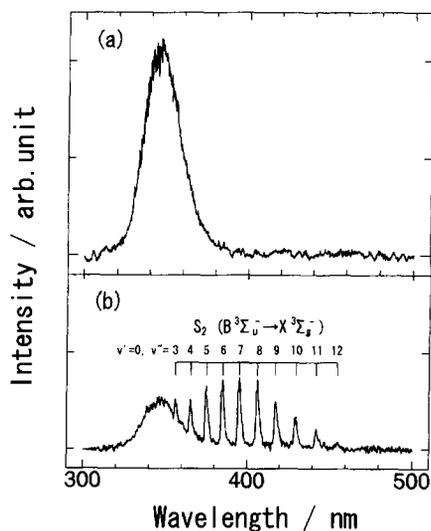


Fig. 1. Emission spectra from OCS-doped Xe crystal excited at 248 nm: OCS/Xe = 1/10000; laser fluence, 0.5 mJ cm $^{-2}$ pulse $^{-1}$. (a) Emission from the irradiated crystal at 17 K. (b) Emission from the crystal after the temperature cycle 17 K \rightarrow 40 K \rightarrow 17 K under irradiation. The structured emission is assigned to S $_2$ (B \rightarrow X) according to Ref. [8].

OCS, a similar broad emission as well as the S $_2$ (B–X) emission were observed. H $_2$ S can yield S atoms on irradiation by 248 nm laser light [2]. In the case of CS $_2$, at first S atoms were isolated and accumulated by the 193 nm ArF excimer laser irradiation, and then the emission induced by the subsequent 248 nm irradiation was investigated. The wavelength and lifetime of the broad emission found in H $_2$ S- or CS $_2$ -doped Xe crystals were, however, slightly dependent on the kind of doped molecules. When CS $_2$

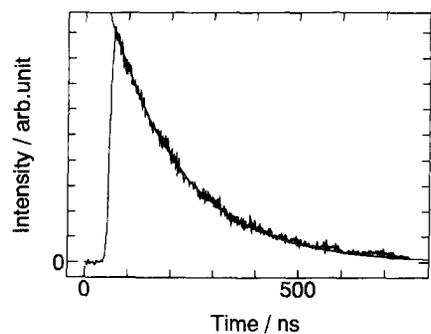


Fig. 2. The time profile of the 346 nm emission intensity: OCS/Xe = 1/10000; laser fluence, 0.5 mJ cm $^{-2}$ pulse $^{-1}$; at 17 K. The single exponential decay curve of 171 ns is also drawn.

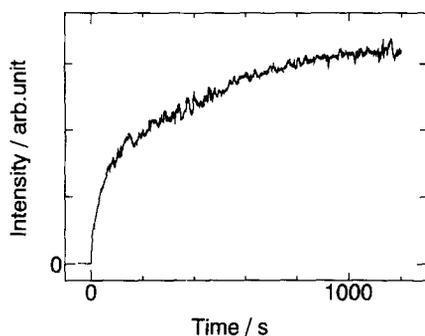


Fig. 3. Growth of the 346 nm emission with irradiation: OCS/Xe = 100000; laser fluence, $3.0 \text{ mJ cm}^{-2} \text{ pulse}^{-1}$; at 16 K.

was employed, the emission maximum was 327 nm and the lifetime was $\approx 110 \text{ ns}$; with H_2S , they were 326 nm and $\approx 120 \text{ ns}$. The features described in the following paragraph were similar to each other among the three different doped molecules. We believe that the emitting species are common for the three precursor molecules, but they may be influenced to some extent by the slightly different neighboring environment caused by the precursor molecules. This is an important problem, but in this Letter we concentrate on describing the features of the broad emission observed in the OCS-doped Xe crystal.

The 346 nm emission was observed to grow on continued irradiation with the KrF laser. A typical growth curve is shown in Fig. 3. It is safe to assume that the 346 nm emission reaches a plateau value when OCS in the irradiated region is consumed. After the plateau was reached, if the crystal temperature was increased to 40 K and kept for a while, the 346 nm emission became weak under subsequent 248 nm irradiation, with stronger S_2 emissions. Similarly, on much stronger laser irradiation than the typical conditions, the crystal temperature increased and the emission of 346 nm decreased with the irradiation time and the $\text{S}_2(\text{B-X})$ emission increased in parallel. Finally only the S_2 emission remained.

The above-mentioned observations are sufficient to establish that the 346 nm emission arises from S atoms, generated by photodissociation of OCS, and destroyed by diffusion-controlled reaction among S atoms to form S_2 . The main dissociation mechanism is expected to be one-photon absorption of OCS, though some OCS may be dissociated through energy transfer from the Xe exciton which may be

prepared via two photon absorption of the 248 nm light. The dissociation of OCS in the gas phase is known to yield $\text{CO} + \text{S}^1\text{D}$. The nascent S^1D may be instantaneously converted to S^3P in the crystal, though the electronic excitation of the S atom at the initial stage may have some effect on the cage exit probability. On the other hand, facile thermally induced diffusion of S atoms in rare gas matrices has been well documented. In fact, the earliest thermoluminescence spectra recorded in matrices are those of S_2 , recorded after VUV photolysis of OCS and CS_2 in matrix Ar [11,12]. Thermoluminescence was also observed in the present study, when the crystal temperature was raised. In contrast with matrices, free standing crystals show large crystal grain sizes, and can therefore be assumed to have long-range order. Thus, the observation of atomic migration in free standing crystals is significant in that it implies migration through the lattice as opposed to grain boundaries, which is commonly implicated in matrix diffusion.

As argued above, the 346 nm emission can be attributed to S atoms isolated in the Xe lattice, though the neighboring environments of the S atoms may be dependent on the precursor molecules, considering that the feature of the broad emission were slightly dependent on the kind of precursor molecule. Intensity dependence studies, as illustrated in Fig. 4, established that the emission was due to direct one-photon absorption, where the 346 nm emission was proportional to the first-order of the irradiating KrF excimer laser intensity, when the laser intensity was varied after the emission reached the plateau value.

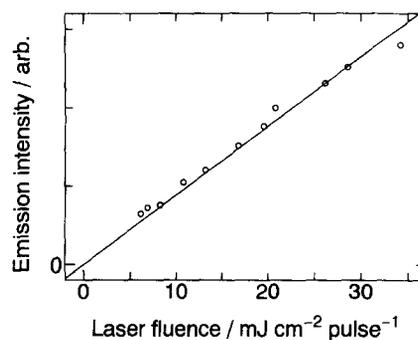


Fig. 4. The dependence of the 346 nm emission intensity on the 248 nm laser intensity. The laser fluence was varied after the plateau was reached: OCS/Xe = 1/1000; at 17 K.

The next question is which state is responsible for the present broad emission. The short lifetime of the emission strongly suggests that it is an allowed transition. The emission energy, 3.58 eV, is much larger than the energy of $S(^1S)$ which occurs at 2.75 eV, and there are no excited atomic states of sulfur in the range of the excitation energy. We are clearly left with the only possibility that the excitation is to charge transfer states between S and Xe host. One candidate is the XeS state corresponding to the state observed in the gas phase by Xu et al. [1], namely, $2^3\Pi$. However, the spin-allowed transition to the ground $1^3\Pi$ state has a large transition energy, 5.46 eV in the gas phase, which is much larger than the present emission energy, 3.58 eV. The stabilization of the upper state by the surrounding Xe atoms is not expected to fully compensate the large difference. A more plausible upper state is then the $3^1\Sigma^+$ state which is the lowest singlet state among the charge transfer states. This state may emit longer wavelength light to reach some of the singlet states which correlate with $Xe + S(^1D)$ or $Xe + S(^1S)$. In the case of O-doped Xe crystal, the 375 nm emission with a lifetime of 227 ns is assigned to the transition from the analogous $3^1\Sigma^+$ state to the $1^1\Sigma^+$ state which correlates with $Xe + O(^1D)$ [6]. More detailed analysis of the excitation and emission mechanism and the consideration of the relevant potential surfaces are now in progress.

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