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Photodissociation of molecular chlorine in xenon matrices

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The photodissociation of Cl₂ in crystalline Xe is examined using synchrotron radiation for all state of Cl₂ from the C $^{1}\Pi_{1\mu}$ state to the region of Xe exciton absorption. Isolation of atomic chlorine in two dominant trapping sites is observed following photodissociation throughout the spectral region studied. The production efficiency of the thermally stable trapping site was found to increase significantly with temperature and was most pronounced in the region of the onset of the Xe₂Cl excitation feature. Correlation between these two processes is explained in terms of a charge-transfer-induced dissociation mechanism involving the formation of a $Xe^+(Cl_2)^-$ intermediate. In contrast to Ar and Kr matrices, photodissociation of Cl_2 in Xe appears to occur without a pronounced cage effect. This observation is rationalized in terms of the larger lattice parameters of Xe which allows isolation of Cl_2 and Cl at single substitutional and octahedral interstitial sites, respectively. From this structural information, simple models are presented for the production of Cl in the two different kinds of trapping sites. Thus production of the thermally unstable site involves the symmetric dissociation of Cl₂ with both Cl atoms occupying octahedral interstitial sites separated by a single lattice constant of Xe. The thermally stable site involves the isolation of one Cl atom at the substitutional site originally occupied by the Cl₂ parent molecule and the other at an octahedral interstitial site.

I. INTRODUCTION

In two previous papers^{1,2} we presented results for the dissociation of Cl_2 in Ar matrices, using the storage ring BESSY as the synchrotron radiation source, and concluded that impulsive cage escape following surface hopping is the dominant mechanism for dissociation in this solid. The present work deals with the dissociation of Cl_2 in Xe for which charge-transfer states and larger lattice constants are expected to play major roles in the dissociation process.

Original interest in the photochemistry of Cl₂ in Xe matrices arose quite indirectly, as it presented a possible means of generating the much sought after molecule xenon dichloride, i.e., Cl-Xe-Cl.³⁻⁵ The relevance of this earlier work to the present study is the method used to generate the species $XeCl_2$, viz., the photodissociation of Cl_2 in Xe and not the formation of the xenon dichloride species itself. It was shown that no photochemistry resulted from excitation with the 514 nm line of the Ar-ion laser while the 501.7 nm line did produce vibrational bands characteristic of the XeCl₂ species.⁴ Assuming that single-photon conditions existed in Andrew's study, both Ar-ion lines reach high vibrational levels in the $B^{3}\Pi_{0\mu}^{+}$ state of Cl₂ (Refs. 6-9) with the 501.7 nm line only slightly above the atomic Cl asymptotes.9 This implies, in contrast to Ar and Kr, 10 that little or no barrier exists for the dissociation of Cl₂ in Xe.

Systematic studies of Cl_2 photodissociation in Xe matrices have come from Apkarian and co-workers,¹¹⁻¹³ who have made extensive use of laser radiation to initiate disso-

ciation. These authors have observed photochemical activity which they attribute to a two-photon, cooperative absorption process reaching a high-lying charge-transfer state between Xe and Cl_2 , from which the dissociation then occurs. To date no experimental work exists using a continuum light source to probe photodissociation in the region of the higher repulsive states, the valence states, or the chargetransfer states of the Cl_2/Xe system. It was with this in mind that the following work was undertaken.

Recently, Gerber and co-workers published results of classical molecular-dynamics (MD) calculations for the dissociation of Cl₂ in solid Xe.¹⁴ The specific system studied was the dissociation of Cl₂ at 3.775 eV in a slab of 107 Xe atoms for which appropriate boundary conditions were set up to model a close-packed lattice of the solid state. Using the XeCl pair potentials of Lee and co-workers,¹⁵ it was found that Cl atom occupancy after dissociation was in an octahedral interstitial site with the second atom remaining at the original substitutional site occupied by the center of mass of the Cl₂ parent molecule. These calculations, in contrast to those on HI in Xe,¹⁶ showed that dissociation at this energy occurred by an impulsive or direct cage exit. Due to orientational effects, permanent dissociation was possible only at elevated temperatures. The predicted dissociation at high temperatures, without a significant cage effect, is in contradiction with the high-pressure investigation of Apkarian and co-workers,¹³ and further experiments at zero pressure are required to resolve these discrepancies.

For the past 20 years, gas-phase studies of the spectroscopy and kinetics of the Cl_2/Xe system have abounded due to the development of excimer-based laser systems.¹⁷ Of these studies, the work of Setser and co-workers¹⁸ will be

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mentioned as it indicated the possibility of the formation of the XeCl molecule from high-lying ion-pair states of Cl₂. Involvement of the ground-state van der Waals XeCl₂ molecule has been inferred by Jouvet and co-workers¹⁹ in the formation of XeCl by a consecutive two-photon process reaching a high-lying state from which the dissociative formation of XeCl occurs. Recently, Janda and co-workers²⁰ published spectroscopic and dynamics data on the XeCl₂ van der Waals molecule which were derived by two-laser pump-probe studies in the vicinity of the $B^{3}\Pi_{0\mu}^{+}$ state of Cl₂. The molecule was found to be "T"-shaped in both the ground and excited states, the former having a well depth of 286 cm^{-1} . These authors comment further on the possibility of reactivity from the B state due to the sharp cutoff of signal for levels having vibrational quantum numbers greater than 12.

The structure of this paper is the following. In Sec. II a brief description of sample preparation is given as well as details of the detection scheme used to monitor photochemistry. The spectroscopy of molecular and atomic chlorine is initially presented in Sec. III as an introduction to the photochemistry which is categorized into the nature of photodissociation efficiency curves and in annealing/temperature effects. Early in Sec. IV the relationship between the excitation spectroscopy of the Xe₂Cl species and the dissociation mechanism is examined. This is followed by a description of the simple models developed in this paper to explain the steps leading to the isolation of Cl atoms in thermally stable and thermally unstable sites. A comparison of the present experimental results with the existing MD calculations on the Cl_2/Xe system concludes the discussion section.

II. EXPERIMENT

The experimental apparatus used in this work has been described in the preceding articles of this series^{1,2} and will not be repeated here. Preparation of Cl_2/Xe samples involved the deposition of gas mixtures having well-defined dilution ratios. The work presented herein involved guest/host dilution ratios of 1:10 000. Samples were deposited at 40 K with flow rates of 0.1 mmol/h and had thicknesses of approximately 50 μ m as measured by interference methods. Spectra were all recorded at 5 K unless otherwise stated.

The spectroscopy used to monitor dissociation of molecular chlorine in matrices has been presented in an earlier paper¹ and only a brief summary will be given here. As for the case of Cl_2 in Ar, detection of atomic chlorine is achieved using the triatomic Rg_2X emission system, i.e., Xe_2Cl with an emission band centered at 570 nm.¹¹⁻¹³ The excitation mechanism in the Xe case is somewhat more complicated than the previously described case of Ar,¹ insofar as the excited state reached in optical absorption for Cl/Xe in the region from 250–350 nm can either be a delocalized electron-hole state^{21,22} or a localized molecular state.^{23,24} The optical cycle for both processes can, however, be generalized by Eq. (1) as follows:

$$\begin{array}{cccc} Xe_{n}Cl & \xrightarrow{\lambda_{ex}} & Xe_{n}^{+}Cl^{-} \\ & & & \downarrow \\ Xe_{2}Cl(1^{2}\Gamma) & \xrightarrow{\lambda_{em}} & Xe_{2}Cl(4^{2}\Gamma). \end{array}$$
(1)

The horizontal arrows in this schematic represent optical transitions while the vertical arrows represent nonradiative relaxation connecting the different levels of the system. The optical cycle in the schematic of Eq. (1) starts for all cases in the upper left with the excitation of ground-state atomic chlorine (indicated by Xe_nCl when isolated in the solid) to an ionic excited state Xe_n⁺Cl⁻. The value of *n* will have values of 1 and 12 for the case of the localized (molecular) and delocalized (hole exciton) systems, respectively. Relaxation of the molecular or electron-hole excited state produces the ionic 4 ${}^{2}\Gamma$ triatomic Xe₂Cl state which radiatively relaxes to the ground 1 ${}^{2}\Gamma$ state. For both systems, emission at 570 nm is monitored, but for excitation, wavelengths at 355 and 332 nm are used for detection of thermally unstable and thermally stable sites, respectively.

III. RESULTS

A. Spectroscopy

Figure 1 shows a typical emission spectrum produced by 308 nm excimer laser excitation of a 0.01% Cl₂/Xe sample. The spectrum as labeled consists of featureless and structured emission bands characteristic of the $4\ ^{2}\Gamma$ -1 $^{2}\Gamma$ and $A'\ ^{3}\Pi_{2u} - X\ ^{1}\Sigma_{g}^{+}$ transitions of Xe₂Cl (Refs. 11, 23, and 24) and Cl₂,^{8,11,12,25} respectively. On the left of Fig. 2, a summary of the low-energy excitation features giving rise to the Xe₂Cl emission at 570 nm is presented. An excitation spectrum recorded at 5 K for the thermally stable site is shown by the solid trace while that of the unstable site is shown by the dotted line. Both spectra were recorded with synchrotron radiation, the dotted line was recorded before and the solid line after annealing of an irradiated sample. The shift in the emission band related to the different excita-



FIG. 1. An emission spectrum produced by the 308 nm XeCl laser excitation of a 0.01% Cl₂/Xe sample. The assignment of the unstructured band centered at 570 nm is Xe₂Cl as shown, while the structured bands extending up to 900 nm correspond to $v' = 0 \rightarrow v'' = n$ transitions in the A-X system of Cl₂.



FIG. 2. Summary spectra of the Xe_2Cl emission recorded using synchrotron radiation. The structured features in the excitation bands (shown on the left-hand side) are transitions to the electron-hole states of atomic Cl in Xe (for the assignment of quantum numbers, see Refs. 21 and 22). The feature-less band shown by the dotted line corresponds to the isolation of Cl in an unstable site. Corresponding shifts in the emission band of Xe_2Cl are shown on the right-hand side.

tion bands is shown on the right of this figure where it is obvious that the thermally unstable site emits with a broad bandwidth approximately 20 nm to the red of the thermally stable site. This behavior has previously been observed and documented by Apkarian and co-workers.¹¹

Excitation spectra of the two emission features shown in Fig. 1 are presented in more detail in Fig. 3 for energies higher than that shown in Fig. 2. The upper panel shows an excitation spectrum of the A-X system of Cl₂ recorded for emission at 859 nm. Structures in the spectral region beyond 150 nm are as labeled, due to absorption from Xe excitons.²⁶ In the middle panel of this figure, an excitation spectrum of the Xe₂Cl emission ($\lambda_{em} = 570$ nm) is shown. The obvious difference between this excitation spectrum and that of the A-X system can be stated as follows: the onset of the former occurs at 190 nm and gradually extends up to the region of the Xe excitons while the onset of the latter is at 220 nm. Assignment of the transitions at wavelengths shorter than 220 nm in the A-X excitations spectrum will be discussed later in relation to the photochemistry of Cl₂ in Xe.

A summary of the spectroscopy of molecular chlorine in the solid rare gases Ne, Ar, Kr, and Xe is shown in Fig. 4, linear in excitation energy, as monitored by the A-X emission of Cl_2 . Depletion features observed in the spectra of Kr and Xe correlate as indicated with the strong and competitive absorption of host exciton bands in these regions.²⁶ Assignment of the excitation features in neon indicate clearly the presence of absorptions to the repulsive $C^{1}\Pi_{1u}$ (Ref. 10) and ${}^{3}\Sigma_{\mu}^{+}$ (Ref. 1) states as well as to the bound 1 ${}^{1}\Sigma_{\mu}^{+}$ ionpair state²⁷ of molecular chlorine. The dependence of the peak positions and intensities of these transitions on the host of isolation can be easily seen by comparing the panels in Fig. 4. Thus the peak positions for the repulsive states show little or no dependence on the host of isolation, while an increase in the relative intensity of the ${}^{3}\Sigma_{u}^{+}$ to the $C^{1}\Pi_{1u}$ state is perceptible on going from Ne to Kr. The intensity relationship between the two aforementioned bands in Xe is not obvious and will be discussed ahead in conjunction with the indication of an additional broad band (C.T). observed to systematically red-shift in matrices on going from Ar, Kr, to Xe.



FIG. 3. Comparison of the excitation features of Cl_2 (top panel) and Xe_2Cl (middle panel) emissions with the photodissociation efficiency curve of the thermally stable site. The emission wavelengths monitored were 856 and 570 nm for the Cl_2 and Xe_2Cl emission bands, respectively. Dissociation at 5 K was monitored by excitation at 332 nm and emission at 570 nm. Absorption features in the *A*-*X* excitation spectrum due to bulk excitons are indicated using the standard notation n = 1, 2, and 1' (Ref. 26), while those due to surface and longitudinal excitons are shown by n_s and n_l , respectively. For assignment of other spectral features see the text.

A demonstration of the effects of annealing on the site occupancy of chlorine atoms after irradiation is given in Fig. 5. Shown in the top panel of this figure is the excitation spectrum of the 570 nm emission band for a sample following 200 shots of XeCl excimer laser irradiation at 308 nm. The emission monitored after sample annealing to 50 K and measured at 5 K is indicated on the same scale directly below in this panel. Clearly, the emission intensity has decreased and the hint of a feature resistant to annealing allows us, as shown by the labels in Fig. 5, to identify features related to thermally stable and thermally unstable sites.

B. Photochemistry

1. Dissociation efficiency curves

As shown in the lower panel of Fig. 3, production of the species labeled "stable" in the Xe₂Cl excitation spectrum is found to increase when the photon energy is increased. As an example, an excitation spectrum recorded after 160 nm synchrotron irradiation of a sample at 50 K is shown in the lower panel of Fig. 5. The resulting structure corresponds to that observed for transitions to the hole–exciton states of chlorine in xenon, the spectroscopy and assignment of which has been given elsewhere.^{11,21,22}

From the spectroscopy of Cl atoms, described in the previous section, we have demonstrated that Cl_2 photochemistry is possible with weak laser fields at 308 nm. Absorption in this region corresponds to transitions from the



FIG. 4. Comparison of the excitation spectroscopy of Cl_2 in the solid rare gases Ne, Ar, Kr, and Xe as monitored by the A-X emission of Cl_2 . Spectra, shown linear in excitation energy, have been corrected for the instrument response function of the excitation monochromator and were all recorded at 5 K for samples having a dilution ratio of 1/10 000. The spectral assignments of Cl_2 , shown for the case of Ne, were taken from Refs. 1, 10, and 27 for the ${}^{3}\Sigma_{u}^{+}$, $C {}^{1}\Pi_{1u}$, and 1 ${}^{1}\Sigma_{u}^{+}$ states, respectively. Exciton assignments were taken from Ref. 26. For a discussion of the charge-transfer states (C.T.) see the text.

ground state of Cl_2 to the $C^{1}\Pi_{1u}$ state for which very efficient "cage effects" have been observed for Cl₂ dissociation in Ar and Kr matrices.^{1,2,10} To confirm that the photochemistry observed in this region was truly single photon and not originating from higher-order processes spuriously induced by laser irradiation, we have repeated these measurements using synchrotron radiation as a light source. The results of these measurements are shown in Fig. 6, where the dissociation efficiency is plotted against the photon energy. Also shown in this plot is the absorption profile of the $C^{1}\Pi_{1u}$ state measured by us. Thus it is clearly evident in this figure that the dissociation efficiency of the unstable site simply follows the $C^{1}\Pi_{1u}$ state absorption profile. An important conclusion to be drawn from this observation is that Cl₂ dissociation from the $C^{1}\Pi_{1\mu}$ state experiences no barrier in Xe, in contrast to the well-documented behavior in Ar and Kr matrices. 1,2,10

2. Annealing and temperature effects

A differentiation is made here between temperature effects induced by annealing and the dependence of the dissociation efficiency upon temperature. Figure 7 makes this dis-



FIG. 5. Demonstration of the effects of annealing on the site occupancy of atomic chlorine after laser and synchrotron irradiation. The effects of annealing on the thermally unstable site are shown in the upper panel where the indication of a thermally stable feature is evident in the lower trace. Prolonged photolysis with synchrotron radiation at a sample temperature of 50 K produces the structured excitation profile shown in the lower panel. The assignment of these structures as progressions of the Cl/Xe hole–exciton states has been given elsewhere (Refs. 21 and 22).

tinction clear where the emission intensity of the thermally unstable site is plotted against temperature. Shown also in this plot is the dissociation efficiency produced by photolysis at 308 nm for five temperature values. Thus, it can be seen that the two processes behave in a very similar way and



FIG. 6. A dissociation efficiency curve of Cl_2 in the region of the $C^{1}\Pi_{1u} - X^{1}\Sigma_{g}^{+}$ absorption leading to the isolation of atomic chlorine in thermally unstable sites. Shown for the sake of comparison is the absorption profile of the A-X transition, scaled to the same peak height, which demonstrates the close relationship between the two processes.



FIG. 7. Temperature dependence of the stability of the "unstable" Cl site compared with the temperature dependence of its production efficiency. The detection scheme involved emission at 570 nm produced by excitation at 355 nm. Laser photolysis at 308 nm, shown by the circles, was performed for constant number of shots at the five indicated temperature values.

what, on first inspection, might be considered a decreased dissociation efficiency with increased temperature, is actually related to the site stability with regard to annealing. This behavior was found throughout the spectral region investigated in this study for the site labeled "unstable" in Fig. 2.

In contrast, the behavior of the thermally stable site was markedly different, viz., the pronounced onset of dissociation occurs at much higher energy, 6.5 eV (190 nm) compared with 3.5 eV (see the bottom trace in Figs. 3 and 6, respectively). It should, however, be emphasized that dissociation leading to the stable site is also possible at lower photon energies although with much lower quantum efficiencies. Figure 8 shows the dependence of the dissociation efficiency of Cl_2 leading to the production of the thermally stable site following weak laser excitation at 308 nm for progressively higher temperatures. Thus, as manifested in Fig. 8, increasing temperature results in enhanced photodissocia-



FIG. 8. Temperature dependence of the production efficiency of the thermally stable site of isolation of atomic Cl in Xe. The photolysis wavelength was 308 nm and dissociation was monitored by excitation at 332 nm with emission at 570 nm.

tion efficiency for the thermally stable site—behavior opposite to that exhibited by the unstable site.

IV. DISCUSSION

A. Spectroscopy and photochemistry of Cl₂ above 5 eV

A summary of the spectroscopy of atomic and molecular chlorine isolated in Xe has been presented in Fig. 3 along with the onset of photodissociation leading to the production of the thermally stable site of isolation of atomic chlorine. The radiative channels which have been monitored in this figure are the A-X system of Cl₂ and the 570 nm band of Xe₂Cl. From this figure a number of features should be noticed. First, the onset of the Xe₂Cl excitation system occurs approximately 1 eV higher than that of the A-X system, 190 nm compared with 220 nm; and second, the onset of efficient production of the thermally stable site of Cl appears to follow the Xe₂Cl excitation spectrum rather closely. In the remainder of this section, we analyze in detail the spectroscopy of the Cl_2/Xe system in relation to the other Cl_2/Rg systems. This allows an identification of purely intramolecular transitions of Cl₂ as well as intermolecular charge-transfer-type transitions. The importance of the latter in the case of Xe is then discussed in relation to the dissociation of Cl₂.

From our experience with the Cl_2/Ar system^{1,2} and given that the $A'^{3}\Pi_{2u}$ state is the lowest excited state of Cl_{2} , 6,10,25 we assume that the structures in the excitation spectrum of the A' - X emission (shown in the top panel of Fig. 3) represent those in the absorption spectrum. The structures shown in the A' - X excitation spectrum at wavelengths shorter than 150 nm originate as labeled, from excitation of the host excitons. The exciton features are indicated in Fig. 3 by the standard notation n = 1, 2, and 1' for bulk excitons and by n_s and n_l for the surface and longitudinal excitons, respectively.²⁶ More interesting, however, in the upper panel of Fig. 3 is the broad band centered at 183 nm (6.8 eV) which has a full width at half maximum of 33 nm (1.0 eV). A similarly broad absorption exists for Cl_2 in the gas phase²⁸ and has to be attributed to transitions into higher repulsive Cl₂ states. This band has also been observed for Cl₂ in Ar and has been attributed to the ${}^{3}\Sigma_{u}^{+}$ state.¹ The oscillator strength of this band in Ar is increased by a factor of 100 compared to the gas phase, and reached a maximum value of $7 \pm 3 \times 10^{-19}$ cm². For the purposes of comparison, the A-X excitation spectra for Cl_2/Ar is shown in the upper middle panel of Fig. 4, along with the corresponding spectra for Cl₂ isolated in Ne, Kr, and Xe. From the systematic observation of this ${}^{3}\Sigma_{u}^{+}$ band in the gas phase, 28 in Ne, Ar, and Kr matrices (see Fig. 4), it is obvious that a corresponding band should also exist in Xe. Thus at least part of the observed absorption probability at 183 nm, shown in the top trace of Fig. 3, must originate from the ${}^{3}\Sigma_{u}^{+}$ state.

There are, however, indications that a further transition is superimposed on the band centered at 183 nm in Xe. It should also be mentioned that while the relative strength of the ${}^{3}\Sigma_{u}^{+}$ band to the $C {}^{1}\Pi_{u}$ band (around 300 nm) increases perceptibly (as shown in Fig. 4) on going from Ne, Ar, to Kr, the band centered at 183 nm in Xe is significantly strong-



FIG. 9. Absorption spectroscopy of the Xe⁺ (Cl₂)⁻ species in solid Xe, trace (a) and in the liquid Xe, trace (b). Trace (a) was recorded in the present study as the excitation spectrum of the *A*-*X* emission of Cl₂ at 859 nm in solid Xe. Trace (b) is taken from the work of Fajardo *et al.* (Ref. 29) and is a portion of the absorption spectrum of Cl₂ in liquid xenon. The dashed line shown immediately under trace (a) was calculated from Eq. (2) using the parameters given in Ref. 29.

er, viz., by about a factor of 8. Fajardo *et al.*,²⁹ using the data of Chen and Wentworth,³⁰ predicted a Xe⁺ (Cl₂)⁻ charge-transfer transition around 180 nm for Cl₂ in xenon. The red wing of this transition has already been observed for Cl₂ in liquid Xe,²⁹ and is reproduced in Fig. 9 by trace (b). The existence of a charge-transfer state in this energy region has been proven by its occurrence also for F₂ and Br₂ in liquid Xe.²⁹ The transition energy E_{CT} to such a charge-transfer state can be estimated²⁹ from

$$E_{\rm CT} = IP(Xe) - EA(Cl_2) + \Delta V(r_c), \qquad (2)$$

with IP(Xe) the ionization potential of Xe, EA (Cl₂) the electron affinity of Cl₂, and the term $\Delta V(r_c)$ which combines the binding and polarization energies of Xe⁺-Cl₂⁻ species. The width of the absorption band is determined in this model by the variation of the "vertical" electron affinity of Cl₂ with the Cl-Cl separation in the vibrationless level of the electronic ground state.³⁰ The shape predicted by Fajardo *et al.*²⁹ using Eq. (2) is represented by the dashed line shown in Fig. 9, and as can be seen, agrees rather well with trace (a), the band recorded by monitoring the *A*-*X* emission of Cl₂. Poorer agreement between the experimental and predicted band shapes especially in the lower energy portion of the $^{3}\Sigma_{\mu}^{+}$ state in Xe which was clearly identifiable at this energy in Fig. 4, for the other rare gases.

The approximate energetic resonance of the ${}^{3}\Sigma_{u}^{+}$ repulsive state and the Xe⁺ (Cl₂)⁻ charge-transfer state in Xe is accidental. In Ar the ${}^{3}\Sigma_{u}^{+}$ state remains, as shown in Fig. 4, at 180 nm, while the Ar⁺ (Cl₂)⁻ charge-transfer states are embedded in the manifold of Cl⁺ Cl⁻ valence states around 10 eV.^{2,27} In Kr, the ${}^{3}\Sigma_{u}^{+}$ state is again observed at 180 nm with the Kr⁺ (Cl₂)⁻ charge-transfer state a well-resolved band between 7.5 and 8.5 eV, i.e., in the region between the ${}^{3}\Sigma_{u}^{+}$ transition and the valence states of Cl₂ beyond 8.5 eV.²⁷ The observed systematic shift of the charge-transfer states in

the different rare gases is, as predicted by Eq. (2) and shown in Fig. 4, mainly determined by the variation of the ionization potentials of the hosts.

One could speculate that the lowest excited Cl_2 valence $1 \, {}^{1}\Sigma_{u}^{+}$ state, which corresponds to a $Cl^{+} Cl^{-}$ ion-pair configuration, is shifted from the gas-phase energy of 8–10 eV down to 6–8 eV in Xe. This seems less likely, however, because as can be seen in the two top panels of Fig. 4, the shift of this state on going from Ne to Ar is only on the order of 0.2 eV and the solvation of the $Cl^{+} Cl^{-}$ dipole is not expected to yield a sufficiently large contribution. A calculation for HCl in Xe (Ref. 31) showed on the other hand, a very strong redshift for the transition energies of Xe⁺ (HCl)⁻ states and an admixture of Cl⁺ Cl⁻ configuration to the Xe⁺ (Cl₂)⁻ charge-transfer state is not excluded.

From Fig. 9 and the previous discussion, it is obvious that the band observed for Cl₂ in Xe at 180 nm represents a superposition of the ${}^{3}\Sigma_{u}^{+}$ state of Cl₂ and the charge-transfer species Xe⁺ (Cl₂)⁻. Both transitions are located at very similar energies and both have similarly large bandwidths of about 1 eV. If we take the value for the ${}^{3}\Sigma_{u}^{+}$ state in Ar of 7×10^{-19} cm² (Ref. 1), and an approximate value of (3-10) $\times 10^{-18}$ cm² for the total absorption cross-section band center from liquid Xe,²⁹ then the dominant part of the absorption cross section belongs to the charge-transfer state.

To be discussed now is whether the repulsive or the charge-transfer state is responsible for the increase of the Xe₂Cl emission and the dissociation quantum efficiency starting around 190 nm. In this context, the correlation between the Xe₂Cl excitation spectrum and the rising of the dissociation efficiency beyond 190 nm ($E_{\text{photon}} > 6.5 \text{ eV}$) (see the middle and bottom panels in Fig. 3) is of prime importance. Only a photon-induced harpooning reaction described by

$$Xe^{+}(Cl_{2})^{-} \rightarrow Xe^{+}Cl^{-} + Cl \qquad (3)$$

can rationalize the direct correlation of the two processes. In this case, the dissociation of the Cl₂ molecule is directly connected with the formation of an excited Xe⁺ Cl⁻ center which relaxes to an excited Xe₂⁺ Cl⁻ center, consequentially decaying radiatively to the neutral ground state by emitting the 570 nm band. The harpooning process for Cl₂/Xe is well known in the gas phase¹⁸ and has been discussed extensively by Apkarian and co-workers^{11,12} for Cl₂ in matrices including the Xe₂⁺ Cl⁻ formation. The high efficiency of the harpooning process with respect to dissociation in solids has been rationalized by Apkarian and co-workers by postulating a negative cage effect for these configurations.¹¹ Thus the similarities in the increase in the Xe₂Cl emission intensity and the dissociation efficiency are a direct signature of the Xe⁺ (Cl₂)⁻ charge-transfer state as a precursor state.

Fajardo and co-workers¹¹ raised the question as to whether the $Xe_2^+Cl^-$ center is formed directly from the $Xe^+(Cl_2)^-$ precursor state or via the Xe^+Cl^- intermediate state [Eq. (3)]. This question can be answered by considering threshold energies involved. Thus the rise of the Xe_2Cl emission intensity (at 190 nm) occurs at significantly higher photon energies than the rise of the absorption band (Fig. 3) which starts at 215–210 nm and which at 190 nm is

already close to its maximum value. This delayed onset displays the energetics involved. The sum of the Cl₂ binding energy of 2.5 eV and the lowest excited Xe + Cl - state of 3.76 eV (330 nm according to Ref. 11) amounts to 6.26 eV (200 nm) and represents the lowest (adiabatic) energy to form Xe^+Cl^- from Cl_2 . The line shape of the precursor $Xe^+(Cl_2)^-$ transition follows from the Cl_2^- electron affinity. An inspection of the $Cl_2^{-2}\Sigma_u^+$ potential curves the Cl-Cl internuclear separation²⁹ shows that the red wing of the transition up to 0.25 eV below its maximum, i.e., 6.65 (1.86 nm) leads to the bound part of the Cl_2^- curve and therefore only at higher energies can the dissociative $Cl_2^- \rightarrow Cl^- + Cl$ portion of the potential be reached. Thus a threshold around 186 nm is expected for the harpooning-type dissociation via the Xe + Cl - intermediate. The close correspondence to the observed threshold at 190 nm suggests that this process is dominant. For the direct formation of $Xe_2^+Cl^-$ the threshold would be reduced by 0.6 eV down to 205 nm due to the smaller $Xe_2^+ Cl^-$ excitation energy (3.1 eV; see Fig. 1 in Ref. 11) and this seems less likely according to the experiment.

It is important to point out that the observation of a preferred dissociation of Cl_2 in Xe via the harpooning mechanism differs qualitatively from the case of Ar. In Ar the dissociation is dominated by a decay of the molecule on the repulsive surfaces and the harpoon reaction which would lead to Ar_2Cl emission was not observed.²

B. Dissociation mechanism

1. Thermally unstable site

An important conclusion of the molecular-dynamics calculations of Gerber and co-workers¹⁴ concerns the site occupancy in Xe matrices of molecular and atomic chlorine on deposition and following dissociation of Cl₂, respectively. Thus using the experimental data of Lee and co-workers¹⁵ for the interaction potential of XeCl, MD calculations show that an ejected Cl atom occupies an octahedral interstitial (I_{ob}) site while the Cl₂ molecule occupies a single substitutional site. The isolation of a Cl atom in an octahedral interstitial site in Xe is easy to rationalize in so far as a Cl atom is only slightly larger than an I_{ob} site. Explicitly, the equilibrium internuclear separation of XeCl in the ground state is 3.23 Å, ^{15,32} and the separation from the center of an I_{oh} site in Xe to the center of a neighboring Xe atom is 3.06 Å.³³ From these packing considerations, the microscopic steps involved in the dissociation of Cl₂ in xenon can be reconstructed, which explains why no barrier is present in this case in contrast to the cases of Ar and Kr. Accordingly, Fig. 10 shows a unit cell of Xe prior to and after the dissociation process.

Starting from the top left panel of Fig. 10, where Cl_2 is shown occupying a substitutional site in the center of the top face, it is easy to see that the isolation of two chlorine atoms in octahedral interstitial sites is possible if the two chlorine atoms move symmetrically upon dissociation. The result of this motion is depicted on the right-hand side of Fig. 10 for which one Cl atom is shown at the I_{oh} site at the center of the fcc unit cell. From symmetry considerations it can be concluded that a corresponding situation exists for the other Cl atoms in the unit cell directly above the one shown in Fig. 10. Since the two Cl atoms in I_{oh} sites are now separated by the lattice constant of Xe [6.13 Å (Ref. 33)] only weak, longrange attractive internuclear forces exist between the two Cl atoms at these distances,³⁴ so that the tendency for their recombination will be small. This proposal is further supported by considering that relaxation around the substitutional site originally occupied by the Cl₂ parent molecule is expected once a vacancy is created there. This structural relaxation, indicated by the arrows on the top of the unit cell, may be a possible explanation for the existence of a small barrier and the resulting thermally activated recombination of Cl atoms following dissociation throughout the spectral region investigated in this study.

2. Thermally stable site

For the stable site, a configuration is required for which recombination is blocked by Xe atoms. The mechanism giving rise to the production of the thermally stable site of Cl isolation begins once again in the top left of Fig. 10. Since the



FIG. 10. Models of the Xe unit cell for the two proposed mechanisms of Cl_2 dissociation in solid Xe, one of which leads to the isolation at thermally stable sites, the other to thermally unstable sites. In the top left of the figure, the initial condition on deposition of a Cl_2 /Xe sample is depicted by the substitution of a Xe atom in the unit cell by a Cl_2 molecule. Following symmetric dissociation of Cl_2 , indicated by the dashed vertical line, the situation shown on the right-hand side is reached. The two Cl atoms now reside at equivalent octahedral interstitial sites separated by 6.13 Å, i.e., the lattice constant of Xe. Collapse of the four atoms surrounding the vacancy created by the dissociation of Cl_2 is indicated by the solid arrows. The unit cell shown on the bottom left depicts the isolation of atomic Cl in thermally stable sites of isolation. The attainment of this situation can be envisioned where one Cl remains at the original site of Cl_2 isolation while the other, whose escape pathway is depicted by the dashed arrows, finally occupies an octahedral interstitial site.

 Cl_2 molecule is constrained with respect to orientational freedom within its substitutional site of isolation, an example for a sufficiently isolated I_{oh} site is shown on the bottom of the unit cell shown in Fig. 10. Allowing one of the chlorine atoms to remain at the original site of Cl_2 isolation, the other Cl atoms must succeed in reaching an octahedral interstitial site, outside the sphere of interaction of the stationary Cl atom. The required motion to reach such a lattice point following an impulsive cage exit involves the movement of one Cl atom nonsymmetrically through the first square of Xe atoms (constituting the lattice atoms situated on the vertical faces of the unit cell) proceeding to one of the I_{oh} sites placed on the bottom of the faces of the unit cell. Such a direct, impulsive mechanism is predicted by MD calculations¹⁴ in which a maximum of two collisions is found in the successful dissociation events. The model proposed here is obviously a very simplified adaptation of the more general MD results. Shown on the bottom of Fig. 10 is the result of such a direct cage escape in which one of the Cl atoms remains at the original site of Cl₂ isolation and the other Cl atom now resides in an I_{oh} site situated slightly more than one lattice constant away.

This configuration corresponds clearly to a thermally stable situation where recombination of the two Cl atoms is highly improbable. The stability of this configuration with respect to annealing is immediately obvious since the recombination of the Cl atoms necessarily involves the passage of one Cl atom through a restrictive triangular window. With the use of the XeCl diatomic potential of Lee and coworkers¹⁵ and the lattice constants of Xe,³³ it can be shown that migration back through such a window imposes a barrier of 0.19 eV. A barrier of this magnitude at the cryogenic temperatures at which these measurements were made is clearly thermally unsurmountable.

C. Comparison with molecular-dynamics calculations

Classical molecular-dynamics calculations for the dissociation of Cl_2 in Xe by Gerber and co-workers¹⁴ have indicated that dissociation occurs by a ballistic mechanism. Thus the orientation of the Cl_2 molecule with respect to the exit cone was found to be the limiting factor controlling dissociation. With increasing temperature the rotational motion of the Cl_2 molecule within its site of isolation accesses orientations favorable for successful cage exit. Because the onset of rotation occurs at high temperatures (95 K) however, dissociation of Cl_2 in Xe₁₀₇ was not predicted to occur within the temperature range of the present experimental study, i.e., 5–50 K. As shown in Sec. III and in contradiction of the theoretical predictions, dissociation of Cl_2 yielding the thermally stable (and unstable) site of atomic Cl isolation is observed throughout this temperature range.

In spite of this quantitative disagreement between theory and experiment it should be noted that the temperature dependence of the dissociation efficiency leading to the production of the thermally stable site does increase with temperature. In Fig. 8 the experimental data are shown and should be compared with the temperature plots of Gerber and co-workers given in Ref. 14. This qualitative agreement may be a manifestation that the rotationally induced mechanism invoked by Gerber and co-workers¹⁴ is operative but that quantitatively it fails due to the inadequacy of the rotational potential used in the MD calculation for Cl_2 in solid Xe.

V. CONCLUSIONS

Photodissociation of Cl_2 in Xe matrices has been observed from all the absorption bands accessible using our experimental apparatus, indicating that a barrier is not operative in the energy region examined, i.e., above 3.4 eV. The observed photodissociation produces atomic chlorine as two spectrally distinguishable species, which from annealing studies allows their assignment as thermally stable and thermally unstable sites. Variation of the photon energy used to initiate the dissociation was found to have a strong influence on the relative distribution of the two sites. Thus at higher energies the production of the thermally stable site was found to increase dramatically at 190 nm, which is the region of the onset of the excitation leading to Xe₂Cl emission.

Consideration of the aforementioned points has led us to the conclusion that what is being observed in the region of the Xe₂Cl excitation spectrum is the onset of XeCl chemiluminescence, which occurs as Xe₂Cl emission in solid Xe. The energetics involved in a vertical transition from the ground state of Cl₂ to a Xe⁺ (Cl₂)⁻ charge-transfer state confirm that chemiluminescence should be observed with the dissociation of Cl₂ in Xe via the production of a Xe⁺ Cl⁻ fragment.

Adopting qualitatively the results of existing moleculardynamics calculations for the dissociation of Cl₂ in Xe, a simple model has been presented, rationalizing the details of the dissociation yielding the thermally stable and unstable sites. Thus the production of the unstable site involves the symmetric fragmentation of the Cl₂ parent molecule residing in a single substitutional site yielding two Cl atoms in the adjacent octahedral interstitial sites. Normally, these sites could be regarded to lead to geminate recombination and are therefore considered trivial with regard to permanent dissociation, but because of (a) the large lattice parameters of solid Xe and (b) the weak intermolecular forces in the $X^{1}\Sigma_{g}^{+}$ ground state of Cl₂ at these distances, the van der Waals XeCl interaction in an I_{oh} site may provide enough stabilization to facilitate trapping. Additional kinetic stability for this site can be understood by considering the constriction of the atoms surrounding the vacancy created by Cl_2 dissociation. This spatial constriction will introduce a small additional barrier to the recombination of the Cl atoms and thus a rationalization of the required stabilization mechanism is possible. Photodissociation of Cl₂ leading to the production of atomic Cl in thermally stable sites has been interpreted in terms of a nonsymmetrical dissociation mechanism where one Cl atoms remains at the original site of Cl, isolation and the other Cl atom finally ends up in an octahedral interstitial site located slightly more than one lattice constant away. This mechanism predicts the isolation of Cl in two distinct types of trapping sites.

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