

Observation of Visible and Infrared Luminescence of Xenon Cluster Ions: Role of Radiative Processes in the Formation of Cluster Ions and their Size and Temperature Dependence

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Observations of continuous luminescence bands in the visible and infrared spectral ranges of Xe_N^+ cluster ions ($N = 10\text{--}2200$) are reported. Based on measured luminescence excitation yields, they are assigned to radiative transitions related to the $^2P_{1/2} \rightarrow ^2P_{3/2}$ transition of atomic Xe ions. The transition energy of one band at ~ 1.9 eV shows a very unusual spectral shift which is proportional to the logarithm of the cluster size, and which can be explained using the Frenkel exciton model. The implications of the size and temperature dependencies for the relaxation processes in ionized clusters are discussed.

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The process of ionization is of fundamental importance in cluster science because only charged particles can be detected with conventional mass spectrometers. A wealth of information regarding the stability, the geometric structure, binding mechanisms, and the shape of clusters has been extracted from mass spectra [1]. On the other hand, it has been known for several years that clusters can undergo heavy fragmentation during the ionization process (which is accompanied by the excitation of internal degree of freedoms) [2]. Fragmentation patterns and measured decay rates have not only been used to obtain information on dynamical processes, e.g., the redistribution of energy in clusters, but also to get information on binding energies [3]. So far, in most of these studies, it is assumed that cluster ions are produced in their electronically ground state although there are some indications that excited states can also be involved [4]. Whether electronically excited levels, e.g., long-lived states, are populated in the relaxation scheme can be analyzed with luminescence spectroscopic techniques.

In this Letter, we report on the first observation of visible and infrared luminescence emission bands in xenon cluster ions. Based on the measured excitation yields they are assigned to radiative transitions from the two lowest electronically excited states to the ground state. These emissions are not only interesting in the context of the redistribution of energy in ionized clusters, but are even more interesting in view of the variation of their transition energy and their intensity with cluster size. The emitting states can be regarded as Frenkel type excitons; in other words, they are directly associated with the corresponding transition $^2P_{1/2}$ to $^2P_{3/2}$ of atomic xenon ions. The transition energy of the band with the higher energy shows an unusual variation with the cluster size. To the best of our knowledge, this is the first example where a variation of a property of a cluster

is observed to be proportional to the logarithm of the cluster size N . In view of the concepts developed (so-called *cluster size equations* [5]), the observed variation of the transition energy falls in the molecular domain where the wavelength of the emitted radiation is much larger than the diameter of the cluster. In other words, the transition to solid state properties, given in this case by the electromagnetic limit, should occur for very large clusters containing more than 10^7 atoms. A theoretical model is developed which accounts for this behavior within the framework of the Frenkel exciton model. In addition, the size dependence of the intensity ratio of the two luminescence bands is analyzed and related to a variation of the cluster temperature with the size of the cluster.

The experiments were performed at the installation CLULU at HASYLAB (DESY) [6]. In brief, Xe_N ($N \propto 2\text{--}2200$) clusters are prepared in a free expansion of xenon gas at a stagnation pressure up to 5 bars at room temperature (300 K) through a conical nozzle ($d = 110 \mu\text{m}$, $2\theta = 30^\circ$). Monochromatized synchrotron radiation (SR) in the range 110–45 nm ($\Delta\lambda_{\text{exc}} = 0.25$ nm) is focused on the cluster beam 15 mm downstream from the nozzle. UV-visible-near-ir fluorescence from the excitation region is analyzed by a 0.25 m monochromator, equipped with an intensified photodiode array detector. Simultaneously, the total VUV (vacuum ultraviolet) fluorescence is detected by a closed (MgF_2 window) channel plate detector coated with CsI. This VUV signal is used for the intensity calibration of the red emissions. For a given stagnation pressure and temperature of the gas, the mean cluster size N has been calculated using the calibration curve from [6].

The main features of the luminescence spectra recorded following selective excitation above the ionization limit of Xe_N^+ clusters concern two new cluster-specific bands,

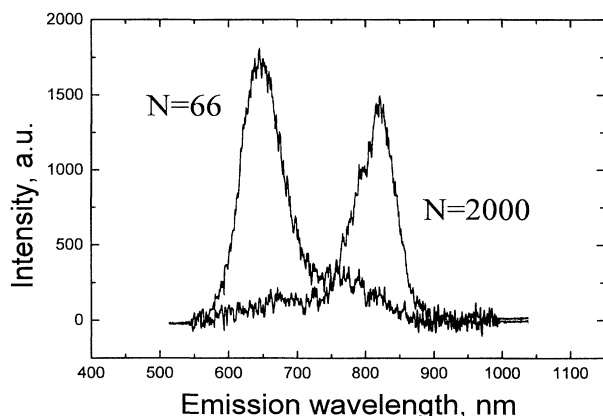


FIG. 1. Fluorescence spectra of Xe_N^+ clusters with $\lambda_{\text{exc}} = 60.0$ nm.

shown in Fig. 1. (1) The first band at $E_1 \approx 1.9$ eV ($\lambda_{\text{lum}} \approx 650$ nm), which appears for $N \geq 10$ and practically disappears for $N \geq 10^3$, has a Gaussian shape with a broad shoulder, on the red side. (2) The second band at $E_2 \approx 1.5$ eV ($\lambda_{\text{lum}} \approx 820$ nm) shows up for $N \geq 200$ in the region of the red shoulder of the 1.9 eV band. It also has an almost Gaussian shape with a small asymmetry towards the blue. Its intensity continuously increases with N . While the first band undergoes a redshift with growing cluster size, no appreciable shift is detected for the second band. The bands were decomposed into a sum of three Gaussian curves, belonging to the 1.9 eV continuum, its red shoulder, and the 1.5 eV continuum, respectively (Fig. 2 shows how the peak of the 1.9 eV emission shifts with N).

In order to make assignments of the different bands, the luminescence yield is recorded as a function of the excitation energy. After excitation above the ionization limit ($5s^25p^5, ^2P_{3/2}$), the VUV fluorescence is caused by

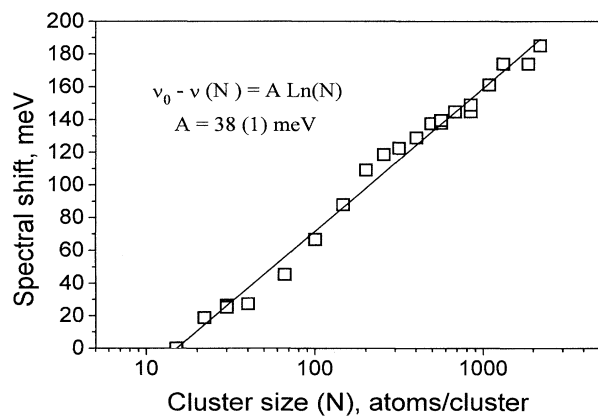


FIG. 2. Spectral shift of the 1.9 eV emission band as a function of the cluster size.

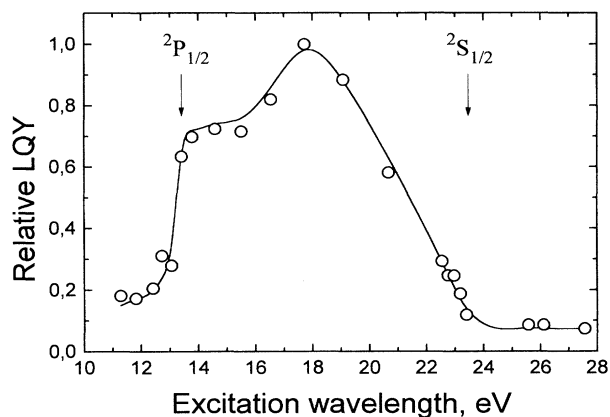


FIG. 3. LQY dependence of the 1.9 eV emission band on λ_{exc} .

the recombination of ejected electrons with cluster ions in the beam. Because each event of recombination gives the VUV photon with a quantum yield of 1, we used the VUV fluorescence signal to normalize the intensities of new emission bands. The luminescence quantum yield (LQY) for the 1.9 eV band is shown in Fig. 3 as a function of the excitation energy. The low- and high-energy limits at 13.4 and 23.4 eV correspond approximately to the ionization energies $5s^25p^5, ^2P_{1/2}$ and $5s^15p^6, ^2S_{1/2}$ (atomic notation). We therefore conclude that the emission bands belong to radiative transitions in Xe_N^+ between states associated with the first excited atomic $5s^25p^5, ^2P_{1/2}$ and ground $5s^25p^5, ^2P_{3/2}$ ionic cores.

We now discuss the nature and the assignments of the emission bands. It should be noted that it is generally accepted that dimer or trimer ionic centers are formed inside the cluster after the ionization has taken place [7]. Therefore, one can hope to interpret the observed luminescence bands using potential energy

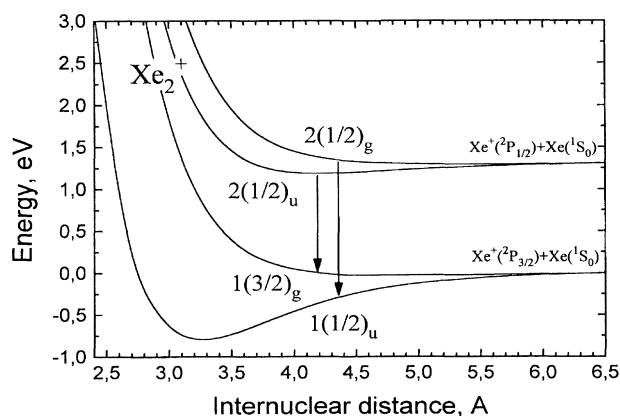


FIG. 4. Schematic drawing of some relevant potential curves of Xe_2^+ .

curves of Xe_2^+ (see Fig. 4). In view of the onset energy required for the appearance of the band, it is obvious that the emissions should be related to transitions between the $5s^25p^5$, $^2P_{1/2}$ and $5s^25p^5$, $^2P_{3/2}$ levels. While $\text{Xe}^+(^2P_{1/2})$ is metastable with a radiative decay time of 48.7 ± 5 ms [8], four transitions from the molecular states $2(1/2)_g$ and $2(1/2)_u$, arising from $\text{Xe}^+(^2P_{1/2}) + \text{Xe}(^1S_0)$, are dipole allowed. The transition energies of two of them, $2(1/2)_g \rightarrow 1(1/2)_u$ and $2(1/2)_u \rightarrow 1(3/2)_g$, which could be considered as candidates, are ~ 1.3 and ~ 1.6 eV [9]. This is considerably lower than the observed values of 1.5 and 1.9 eV.

The disagreement can be solved if one considers that larger ionic units are formed in clusters. As shown by model calculations [10], the most stable structures of the hole inside the Xe_N^+ cluster are linear Xe_3^+ and Xe_4^+ . Xe_3^+ is bound by 0.36 eV with respect to $\text{Xe}_2^+ + \text{Xe}$. Roughly, $\delta E_h \approx 0.25$ eV is due to a charge delocalization, and 0.11 eV is due to polarization forces. Xe_4^+ is bound by only 0.15 eV with respect to $\text{Xe}_3^+ + \text{Xe}$, where the polarization interaction dominates. The polarization interaction (charge-induced dipole) does not change for the ground and excited ionic states. On the other hand, only the ground state potential is influenced strongly by this extra stabilization that is due to a hole delocalization on the third atom. This is why the low-energy threshold of the excitation spectrum of Xe_N^{+*} clusters fits the $5s^25p^5$, $^2P_{1/2}$ level position (Fig. 3), while the ionization potential decreases with N . Therefore, one could expect an increase by δE_h in the energy corresponding to the $2(1/2)_u \rightarrow 1(3/2)_g$ transition, giving the transition energy of $1.3 + 0.25 = 1.55$ eV. This is in agreement with the energy of the second emission band. In view of this discussion, the first red emission band could be related to the $2(1/2)_g \rightarrow 1(1/2)_u$ transition ($E_2 \approx 1.66 + 0.25 = 1.91$ eV). It is free bound in dimer ions. However, in clusters, the $2(1/2)_g$ excitonic state can be stabilized due to the polarization interaction of the hole with its surrounding atoms.

The inset in Fig. 5 shows the intensities of the two emission bands as a function of N . Surprisingly, the intensity of the 1.9 eV band decreases for $N > 100$, while the intensity of the 1.5 eV band starts to increase at the same cluster size. In the following, we show that the variation of the intensity ratio can be related to the variation of temperature of Xe_N^+ clusters. The basic idea comes from our assignment of the emitting states: The $2(1/2)_g$ state, for which the emission at 1.9 eV starts, weakens with lower temperature because it is energetically above the $2(1/2)_u$ state which emits at 1.5 eV. In a crude approximation, the cluster temperature (T_{cl}) drops with N as $1/2kT_{cl} = 1/2kT_{cl}^0 + E_{dep}/(3N - 6)$, where E_{dep} is the energy deposited in the cluster. Therefore, the population (p_1) of the more energetic $2(1/2)_g$ state will decrease with an increase of the cluster size relatively to the $2(1/2)_u$ state population (p_2) as

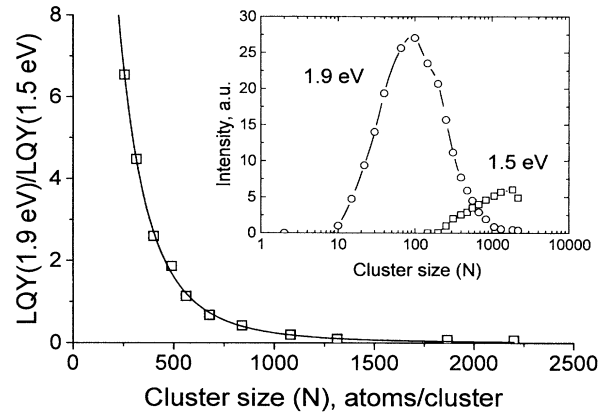


FIG. 5. LQY's ratio of two red emission bands on the cluster size. The LQY dependences on the cluster size are given in the inset.

$$p_1/p_2 \propto \exp(-\Delta E_{1,2}/kT_{cl}) \\ \approx \exp\left(-\frac{1.5\Delta E_{1,2}}{1.5E_{dep} + kT_{cl}^0 N} N\right)$$

($\Delta E_{1,2}$ is the energy gap between the two emitting states). The fit by this function is given by the solid line in Fig. 5. As we see, p_1/p_2 does indeed show a Boltzmann distribution. Because either E_{dep} or $\Delta E_{1,2}$ are also functions of N , we can estimate these values for a limited range of cluster sizes. From the fit, and assuming a cluster temperature of 80 K [11], we get $\Delta E_{1,2} \approx 50$ meV and $E_{dep} \approx 5$ eV. The deposited energy $E_{dep} \approx 5$ eV is somewhat lower than the difference between the excitation ($h\nu_{exc} = 20.67$ eV) and excited state energies, 8 eV. It illustrates that $\sim 60\%$ of the excess energy is transferred to the cluster. In other words, inelastic scattering processes, which lead to fragmentation of clusters, can, under certain conditions, play a stronger role than previously assumed [8].

Another very interesting aspect is the variation of the measured transition energy of the first emission band (~ 1.9 eV) presented in Fig. 2. In view of the theoretical results discussed below, the spectral shift is displayed on a logarithmic scale for N . In the following, we apply the Frenkel exciton model which describes the transition of strongly localized centers in molecular crystals to the emission of xenon ionic clusters. The transition energy from the ground to the excited (f) state is expressed in the Frenkel exciton model by [12]

$$E_f(\mathbf{k}) = \Delta \epsilon_f + D_f + L_f(\mathbf{k}), \quad (1)$$

where \mathbf{k} is the exciton wave vector, $\Delta \epsilon_f$ is the transition energy of a free molecule, D_f is the change in the interaction energy of one molecule with all of the surrounding atoms, and

$$L_f(\mathbf{k}) = \sum_m M_{nm}^f \exp[i\mathbf{k} \cdot (\mathbf{n} - \mathbf{m})] \quad (2)$$

is the resonance interaction term that involves the matrix element M_{nm}^f of the excitation transfer between molecules n and m . Usually the Frenkel exciton model is used to describe absorption processes. However, in our particular case, it can also be applied to the description of the emission, assuming that the geometry of the excited ionic state (i.e., the internuclear separations) is nearly identical with that of the ground state. The emission originates from "sufficiently large" clusters with complete first-shell neutral atoms around the excited hole ($N > 10$). Therefore, it is the interaction with distant atoms of $n_{\text{shell}} \geq 2$ which causes the observed energy shift of the excited hole (presumably Xe_3^{+*} or Xe_4^{+*}). The excited hole has no permanent dipole moment, and its interaction with the surrounding atoms is almost the same as in the ground state configuration of Xe_3^+ (Xe_4^+) (which is taken for the excited state geometry). In this case, it is reasonable to assume that $\delta D_f(N) = 0$. $\Delta \epsilon_f$ is not a function of N , and therefore the spectral shift is determined solely by the $\delta L_f(N)$ term. $L_f(N)$ is due to a transition multipole of the emitted center. In case of dipole-dipole interaction, M_{nm}^f is expressed by

$$M_{nm}^f = \frac{1}{r_{nm}^5} [(\mathbf{d}_n \mathbf{d}_m) \mathbf{r}_{nm}^2 - 3(\mathbf{d}_n \mathbf{r}_{nm})(\mathbf{d}_m \mathbf{r}_{nm})], \quad (3)$$

where $d_n = d_m = d/\sqrt{\epsilon}$, and $\epsilon = 2.1$ is the dielectric constant of solid xenon (see [13]).

If the size of the Xe_N clusters is small compared to the wavelength of the emitted light ($R_{\text{cl}} = N^{1/3} r_0 < \lambda_{\text{lum}} = 650 \text{ nm}$), the term $L_f(\mathbf{k})$ can be calculated by replacing the summation in (2) by an integration of different contributions of M_{nm}^f . We obtain

$$\delta \nu(N) = -\alpha \frac{d^2}{3\epsilon r_0^3} \ln(N), \quad (4)$$

where the numerical constant $\alpha = 4.140$ [$r_0 = (3/4\pi\rho)^{1/3} = 0.240 \text{ nm}$; ρ is the solid density].

A least squares fit of the experimental data in Fig. 2 (shown by the solid line) gives $\delta \nu(N)/\text{meV} = -38 \ln(N)$. From this and (4), the strength of the transition dipole can be determined to $d = 0.445 \text{ a.u.}$ It is in agreement with values of 1.1–0.5 a.u. for the dipole moment of the $2(1/2)_g \rightarrow 1(1/2)_u$ transition of Xe_2^+ at the relevant internuclear distances [9]. The second emission, which is related to the $2(1/2)_u \rightarrow 1(3/2)_g$ transition in xenon dimer ion, exhibits no appreciable shift with cluster size: $|\delta \nu_2| \leq 15 \text{ meV}$. Presumably, the resonant transfer term $L_f(\mathbf{k})$ in (1) is lowered because the bound length in the $2(1/2)_u$ state is smaller than in nondistributed lattice, and also the transition moment is lower. An alternative explanation would be that this

band is due to an emission from a stable cluster ion (e.g., Xe_{55}^+), which is formed during the ionization process across a wide range of cluster sizes.

We would like to point out that a cluster size equation, which shows a proportionality to $\ln(N)$, has been obtained recently for the change of radiative lifetimes with the cluster size [14]. The results for transition energies of Xe_N^{+*} cluster presented here are, however, the first proof showing that a logarithmic dependence can indeed be observed. Furthermore, it should be noted that these quantities can only be calculated for clusters, since for macroscopic solids the summation over M_{nm}^f in Eq. (2) diverges.

In conclusion, we have observed two emission bands in Xe_N^+ clusters which are interpreted within the Frenkel exciton model assuming Xe_3^{+*} or Xe_4^{+*} emitting centers.

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