

Condensation and Light Emission

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Abstract— Light emission in the condensation of noble gases at low pressure containing clusters of silver atoms is thought caused by the radiative loss of the excess in binding energy as the clusters agglomerate. Deposition of silver clusters on a cold cryogenic substrate produces a spectrum with visible (VIS) emission lines in the blue and red with the intensity of the emission significantly influenced by the substrate temperature and whether dimer or trimer atoms are agglomerated. At 30K, the dimer atoms dominate with the color of the VIS emission blue-violet, but during agglomeration as the substrate warms to 50K the trimer atoms dominate with the VIS emission continuously changing to a red color. It is likely, therefore that VIS emission is driven by temperature as a significant change in binding energy of the dimers and trimers during warming of the substrate is unlikely. An alternative VIS light emission mechanism is proposed based on the infrared (IR) radiation at cryogenic temperatures from the atoms in the clusters whereby the gap is treated as an electromagnetic (EM) cavity. As the clusters approach each other, the gap between the clusters is first sufficiently large and the IR radiation from surface atoms freely emitted. As the gap closes, the electromagnetic (EM) resonance of the QED cavity increases from IR to VIS frequencies, and therefore the lower frequency IR radiation from the surface atoms is suppressed. Suppressed IR radiation is a loss of EM energy that can only be conserved by a spontaneous and equivalent gain at the instant resonant EM frequency of the QED cavity, the process called cavity QED induced EM radiation. In this way, the suppressed IR radiation is progressively frequency up-converted from the red to the blue. At 30K, the VIS emission is predominantly blue, but has a low intensity compared to that at 50K because of the lower kT energy of the atoms while the spectrum is broadband because of the random distribution of EM resonances in the gaps between the surfaces of the agglomerating clusters.

Introduction

Light emission accompanying the condensation of small Ag clusters in an Ar gas [1-4] on the surface of a cryogenic plate is usually explained by the excess energy from the binding of the Ag clusters. The Ag clusters emit a broadband spectrum with the more intense spectral lines associated with the known lines of Ag atoms, dimers, and trimers. However, there may be a problem with this theory because the concentrations of Ag clusters in the mixture is less than 1 % of that of the Ar gas, and therefore the Ag clusters are shielded from each other so that binding is precluded, and therefore excess energy during condensation is unlikely.

Here a different theory is proposed. Because of the small concentration of Ag clusters in the Ar gas, the Ag clusters are treated as impurities in an otherwise pure Ar gas which condenses to a liquid. If the Ar gas to liquid condensation could somehow provide a source of EM radiation, the Ag clusters as impurities would be excited to produce the light emission and thereby explain the observed spectral lines of Ag atoms and its dimers and trimers.

Indeed, EM radiation is produced during the condensation of Ar gas to liquid. IR radiation from Ar atoms on the surface of collapsing nanovoids is suppressed to produce VUV radiation by a process called cavity QED induced EM radiation. Here, QED stands for quantum electrodynamics. By this process, the condensation of vapor occurs as a heterogeneous mixture of liquid and evacuated nanovoids that forms adjacent the cryogenic plate. In fact, light emission from Ag clusters is similar to the light from impurities in cryogenic liquids after a vapor bubble produced by the heat of a laser (see *SL in Cryogenic Liquids* in [5]) collapses. For Ag clusters in condensing Ar gas, the nanovoids are treated as momentary QED cavities that suppress the IR radiation from the Ar atoms in the cavity walls including the Ag cluster impurities. Cavity QED induced EM radiation is illustrated for one of a large number of nanovoids during the condensation of Ar gas in Fig. 1.

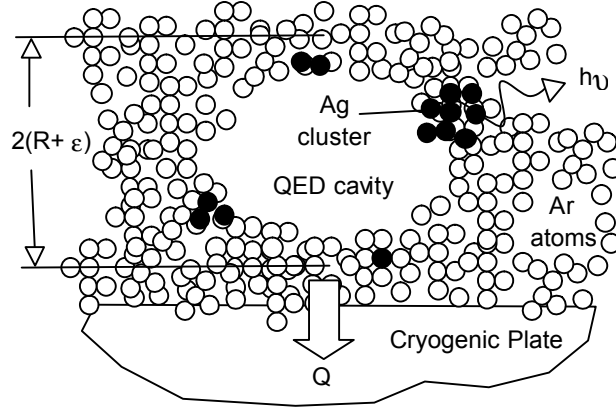


Fig. 1 Condensation of Ar gas including Ag clusters

In the Ar gas condensation, heat Q is extracted by the cryogenic plate to form evacuated QED cavities in the liquid during matrix growth. The QED cavities are of arbitrary shape, but are represented by spherical geometry of radius $(R + \epsilon)$ having a resonant wavelength $\lambda = 4(R + \epsilon)$. Here, ϵ is the penetration depth of the VUV radiation into the QED cavity wall. The QED cavities may be considered evacuated because of the low vapor pressure of Ar at cryogenic temperatures. The Ag clusters comprising a number n of Ag atoms, dimers, and trimers are shown in the QED cavity wall within the penetration depth ϵ .

In cavity QED induced EM radiation, the IR radiation from atoms within the penetration depth is suppressed [5] because the EM resonant frequency of the QED cavity is higher than IR frequencies, or the half IR wavelength is greater than the bubble diameter $2(R + \epsilon)$, i.e., $\lambda/2 > 2(R + \epsilon)$. The QED cavities are submicron and as such, the resonant frequency is taken beyond the VUV. For a spherical QED cavity resonant in the VUV, the EM energy U_{IR} loss by suppressed IR radiation is,

$$U_{\text{IR}} = \frac{4\pi}{3} \Psi \left[(R + \epsilon)^3 - R^3 \right] \quad (1)$$

where, Ψ is the EM energy density, $\Psi \sim N_{\text{dof}} \times \frac{1}{2} kT / \Delta^3$, and Δ is the cubical spacing between Ar atoms at liquid density. N_{dof} is the number of degrees of freedom, for noble gases, $N_{\text{dof}} = 3$. Hence,

$$U_{\text{IR}} = 2\pi \left[\left(\frac{R + \epsilon}{\Delta} \right)^3 - \left(\frac{R}{\Delta} \right)^3 \right] kT \quad (2)$$

Since the EM energy loss must be conserved by an equivalent energy gain, and since the lowest frequency admissible in a QED cavity is at its resonant EM frequency, the suppressed IR is frequency up-converted to the VUV. The Planck energy E_{avg} of the VUV photons in the penetration depth ϵ is,

$$E_{\text{avg}} = \frac{hc}{4(R + 0.5\epsilon)} \quad (3)$$

Combining, the number N of photons having Planck energy E_{avg} produced in the penetration depth ϵ ,

$$N = 4\pi \frac{kT}{hc} (R + 0.5\epsilon) \left[\left(\frac{R + \epsilon}{\Delta} \right)^3 - \left(\frac{R}{\Delta} \right)^3 \right] \quad (4)$$

Typically, the QED cavities are resonant in the far IR, and during agglomeration the EM resonance increases first to the near IR, and then VIS, and finally to the VUV. If the liquid Ar is absorptive but does not ionize, then at any instant the number N and average Planck energy E_{avg} are conserved,

$$U_{\text{IR}} = NE_{\text{avg}} = N_{\text{NIR}}E_{\text{NIR}} = N_{\text{VIS}}E_{\text{VIS}} = N_{\text{VUV}}E_{\text{VUV}} \quad (5)$$

In the application to the condensation of Ar gas, the absorption coefficient α over the wavelength range from about 10 to 120 nm is required, but not known. For water, the peak α is about 1×10^8 /m at $\lambda \sim 80$ nm as shown in Fig. 3 of [5]. The penetration depth ϵ is then found by taking $\alpha\epsilon = 5.15$ which corresponds to 99% of the EM energy absorbed. For water, $N \sim 2 \times 10^5$ at $E_{\text{avg}} \sim 8.3$ eV or $4(R + 0.5\epsilon) \sim 150$ nm. For $\epsilon \sim 40$ nm as shown in Fig. 6 of [5], $R \sim 18$ nm.

Discussion

Analysis of the QED cavity requires the absorption coefficient α of liquid Ar following the procedure given in [5]. Here, the discussion is made as to whether cavity QED induced EM radiation is consistent with the data for light emission in the condensation of Ar gas containing Ag clusters.

Comments on Science [1]

Similarity with Chemiluminescence by Chemical Reaction

Cavity QED induced EM radiation is similar to chemiluminescence by chemical reaction.

“Exothermic chemical reactions may be accompanied by chemiluminescence. In these reactions, the released energy is not adiabatically damped into the heat bath of the surrounding medium but rather is stored in an excited state of the product while decay from this excited state to the ground state is associated with light emission.”

In a comparative restatement: In a vanishing QED cavity, suppressed IR from surface atoms may be accompanied by light emission as the EM resonance of the collapsing QED cavity passes through VIS frequencies. The suppressed IR is not converted to heat because any increase in temperature of the surface atoms corresponds to IR radiation which is inadmissible in the higher EM resonant QED cavity, but rather is stored in an excited state of the surface atoms at the EM resonant frequency of the QED cavity. Light emission in the VIS occurs if the EM frequency of the vanishing QED cavity coincides with the VIS and the walls of the QED cavity are transparent at VIS frequencies.

Significance of Temperature

“The temperature of the noble gas matrix (as determined by the substrate temperature) had a significant influence. At higher temperatures, luminescence was observed continuously during deposition, whereas the intensity was much weaker at lower temperatures; however, in the latter case subsequent warming then initiated high light emission. These findings indicate that the observed light emission is a consequence of the agglomeration of clusters inside the noble gas matrix; this process requires the temperature to be high enough to warrant sufficient mobility”

In cavity QED induced EM radiation, temperature is important in defining the available thermal kT energy of Ar atoms the IR radiation of which is suppressed in the QED cavity. Thus, the light intensity is weaker at lower cryogenic Ar temperatures, but on subsequent warming the light emission increased. By this theory, mobility of Ag clusters is not the reason for the increased light emission with temperature.

Effect of Noble Gas

“Coalescing Cu clusters emitted light in two characteristic spectral regions (Fig. 2). Variation of the noble gas had only a minor influence on the spectral characteristics. However, Ne presented the less perturbing medium, and therefore, vibrationally resolved spectra, for example, of dimers can be easily obtained in a Ne matrix... (Fig. 2A) ... The broad emission is attributed to Cu_n clusters ($n > 3$)”

Cavity QED induced EM radiation is a broadband excitation source from the NIR through the VIS to the VUV. Spectral lines superpose on the broadband background if a chemical species present in the liquid is excited, e.g., clusters and dimers or trimers of Ag or Cu. Since the broadband excitation is continuous, all modes from the NIR to the VUV are excited. What is shown in Fig 2A and 2B is the superposition of spectral lines on the broadband background, the latter lower in intensity for Ne than Ar.

Comments on JCP [2]

Light Emission and Size of Clusters

“Continuous luminescence was also observed during the deposition at temperatures high enough to allow migration and agglomeration of the condensing species. No light emission was, however, observed if the deposited clusters were larger ($n > 20$) and if monomers and dimers were missing. These findings suggest that chemiluminescence is essentially caused by clusters in the intermediate size range, viz. $3 < n < 20$.”

In cavity QED suppression of IR radiation, the EM radiation is frequency up-converted in the Ar atoms is absorbed within the penetration depth ϵ of the QED cavity wall. But ϵ may be large compared to the radius R of the evacuated void. By this theory, light emission cannot occur if the cluster radius $R_c >$ the void radius R . For 20 Ag atoms, $R_c \sim 0.4$ nm. As shown above for water, $\alpha \sim 1 \times 10^8$ /m at 8.3 eV or $R + 0.5 \epsilon \sim 37.5$ nm that for $\epsilon \sim 40$ nm gives $R \sim 18$ nm. For liquid Ar, α is not known, but if $\alpha < 1 \times 10^8$ /m, $\epsilon > 40$ nm and $R < 18$ nm. E.g., if $\alpha \sim 5 \times 10^7$ /m, $\epsilon \sim 80$ nm and $R \sim 0$ nm. Depending on the absorption of Ar, the Ag cluster size may exceed the QED cavity radius R , i.e., $R_c > R$. If so, light emission for larger Ag clusters cannot occur. The data suggests this occurs if the Ag cluster has more than 20 atoms.

However, the limit on the Ag cluster size of 20 atoms may be related to the morphology of the formation of the Ar matrix and have nothing to do with the absorption coefficient α of liquid Ar. To resolve this issue, α data for Ar is required and the analysis performed as described for water in [5].

Light emission is stated not to occur if monomers and dimers were missing. This is correct only for VIS light. Fig 3 of [2] shows the spectral lines of Ag_2 and Ag_3 to dominate, and if the monomers and trimers were missing, the light emission would not occur. But the NIR emission may still exist. Cavity QED radiation exists independent of whether monomers and trimers are missing, although at a low background level. Table 1 of [2] shows for $n > 1$ the response of Ag clusters to QED radiation that is not dependent on monomers and trimers.

Discrete and Continuous Excitation Sources

“Figure 5(a) compared this band (sic 476 nm) with the light emitted from Ag_2 clusters in a Ne matrix upon excitation with monochromatised light ($\lambda=425$ nm) from a xenon lamp. The practically identical peak positions and vibrational splitting are clear indications for the assignment of this chemiluminescence band to Ag_2^* species.”

Conversely, Fig. 5(a) of [2] shows the significant differences in the response of Ag_2 in a Ne matrix to photo induced emission (425 nm) and chemiluminescence by continuous cavity QED induced radiation. The peak positions are not identical because of the continuous nature of QED induced EM radiation source excites the Ne matrix differently than possible with the photo induced source at 425 nm. A random excitation source centered at 425 nm may provide a better comparison with the chemiluminescence spectrum.

Light Emission Mechanism

“The results presented support the previously proposed mechanism leading to light emission⁶. Any spurious effects leading to energy supply, such as interference with electrons or ions, chemical reaction with impurities or cavitation associated with the collapse of local bubbles, can be ruled out, so that we are left with the energy gain accompanying agglomeration of small clusters to larger ones as the source for excess energy leading to electronically excited states decaying with the emission of photons.”

With regard to the light emission mechanism, the excess of energy accompanying agglomeration of small Ag₂ dimers into larger Ag clusters has the fundamental difficulty that the emission is required to depend on the Ag cluster to which it is binding, and although possible is a difficult physical constraint for any photon mechanism. Fig. 5a of [2] shows this difficulty because the peaks in the photo induced emission at 425 nm from Ag₂ in a Ne matrix do not coincide with the chemiluminescence response. This means that more than one photo induced excitation frequency is necessary to produce chemiluminescence, but how this other frequency or even a range of frequencies are produced in binding is not explained.

Instead of the photo induced emission from Ag₂ dimers in Ne matrix, the emission from isolated Ag₂ dimers should be presented, and if so, the spectra¹ should coincide in the location of the peak chemiluminescence, although in the chemiluminescence spectrum a broadening about the peaks is expected because of the surrounding liquid Ne.

Cavitation associated with the collapse of local bubble with an increase in temperature may be safely ruled out as a light emission mechanism. But a vanishing evacuated QED cavity or the closure of gaps between incoming Ar gas and the Ar matrix suppresses IR radiation from the surface Ar and Ag atoms, thereby inducing light emission from the electronic states of the Ag clusters.

“According to *ab initio* calculations, the binding energy of Ag₂ (i.e., the excess energy of the process $\text{Ag} + \text{Ag} \rightarrow \text{Ag}_2$) amounts only to 1.6 eV¹⁴, and hence an Ag₂* species which subsequently decays into Ag₂ by emitting a photon with $h\nu = 2.6 \text{ eV} (=476 \text{ nm})$ is not feasible. Obviously the energy balance can only be fulfilled if a large number of bonds is formed, that means if larger clusters are involved. ...On the other hand there exists a series of data for *ab initio* calculations for ground state properties of small Ag clusters, from which the overall reaction enthalpy can be composed... These numbers are not yet completely fulfilling... but it is felt that with somewhat larger clusters the energetic requirements may be fulfilled.”

The problem is not with the energy balance in larger clusters, but rather how the excess binding energy is released in a continuous manner with frequency. If a continuous range of excitation frequencies in photo induced emission is required to explain the light emission, it is far simpler to rely on cavity QED induced EM radiation that simply uses the suppressed IR in the surface atoms in incoming Ar gas at large separations to excite higher frequency modes as the QED cavities or gaps vanish.

Comments on *Chem. Phys. Lett.* [3]

Relation of Ag to Ar Atoms in Pick-Up Technique

“In contrast to findings with clusters embedded into noble-gas matrices, silver trimers were found to be by far the most abundant excited species formed by the agglomeration process. Their chemiluminescence spectrum is markedly affected by the neighborhood of noble-gas atom. The latter evaporate, however, continuously by the heat released by the condensation and coagulation process, so that

¹ In sonoluminescence of K in alcohols [6], the spectral peaks coincide with the K spectra from a hollow cathode lamp in a vacuum, although the sonoluminescence spectrum is broadened because the emission is produced in the liquid state.

under suitable conditions even chemiluminescence from ‘naked’ Ag_3^* clusters could be observed.”

The fact that the chemiluminescence spectrum is affected by the neighborhood of the Ar atoms poses another difficulty because the theory for photon emission by excess binding energy does not depend on the proximity of the Ar atoms. Only in the limiting case where chemiluminescence is observed from ‘naked’ Ag_3^* clusters formed as the Ar evaporates is the excess binding energy applicable. But even then cavity QED induced radiation applied to QED cavities in the solid state formed in the Ag clusters as the Ar evaporates explains the light emission. The importance of Ar in Ag light emission is overwhelming.

“The emitted light was found to change its color with variation of the Ar stagnation pressure, i.e., cluster size. This is reflected by the emission spectra reproduced in Fig. 2 for $p = 2, 6,$ and 10 bar, corresponding to about $n = 40, 300,$ and 750 Ar atoms/cluster, respectively.”

Cavity QED induced EM radiation is also applicable to the chemiluminescence from Ag clusters picked-up as the Ar droplets produced in the nozzle expansion form evacuated QED cavities that provide the excitation source for Ag clusters. That the Ar droplets are the source of the excitation producing light emission from Ag clusters follows from the fact that light emission is not observed from vaporizing Ag in the absence of the Ar droplets.

Light Emission occurs from different Electronic States

“Fig. 4 shows this emission spectrum together with the photo induced fluorescence spectrum of Ag_3 centered around 500 nm. The latter was created by irradiation of the cluster beam with white light...By contrast, the chemiluminescence spectrum shows up at somewhat longer wavelength and is broadened with vibrational fine structure appearing only as shoulders. This indicates that light emission occurs from different electronically excited states.”

In Fig. 4 of [3], the similarity of photo induced emission excited with white light and the chemiluminescence from bare Ag_3 clusters suggests the chemiluminescence is occurring from different electronically excited states. The white light spectrum is consistent with the excitation of discrete vibrational levels from an external source; whereas, the chemiluminescence spectrum lacking discrete vibrational levels is consistent with the excitation of vibrational levels damped in the liquid state from an internal emission source, e.g., similar to sonoluminescence. But what is the internal source that excites the different electronic states in chemiluminescence?

Cavity QED induced EM radiation is a source of internal excitation for chemiluminescence as Ar clusters pick-up Ag clusters. Even if the Ar atoms are stripped from the Ag_3 clusters, the Ag_3 clusters still are vanishing QED cavities in the solid state that are closing upon agglomeration. If so, light emission occurs without Ar atoms. But the spectrum for bare Ag_3 clusters is expected to be different from that of Ag_3 clusters in Ar droplets.

Comments on *Chem. Phys. Chem.* [4]

Light Emission depends on Ar concentration

“At first sight somewhat unexpectedly, the intensity of chemiluminescence was found not only to depend on temperature and deposition rate of silver, n_{Ag} , but also on that of argon, n_{Ar} . This becomes evident from inspection of Figure 4 which shows the intensity of Ag_3^* emissions as a function of n_{Ag} for various n_{Ar} at 10K (a) and 30K (b), respectively. Variation of n_{Ar} by one order of magnitude causes an increase of the maximum intensity by more than a factor of $100!$ Figure 5 shows a plot of this maximum intensity at 30K as a function of n_{Ar} . These data explain why under normal matrix isolation conditions with typical gas deposition rates of the order of

10^{16} atoms $s^{-1} cm^{-2}$, chemiluminescence has never be observed because of low intensity.”

The difficulty with excess binding energy of Ag clusters as the explanation for light emission is perhaps best illustrated in Figs. 4 and 5 of [4] that light emission is very sensitive to the concentration of Ar atoms, and therefore the concentration of Ar somehow causes the light emission in Ag clusters. But the binding energy explanation is independent of the Ar concentration. Moreover, if the Ag concentration exceeds about 1 % of the growing matrix, the situation becomes unstable suggesting that the concentration of Ar and not Ag is important in light emission.

“At 10 k the intensities of emitted light increase continuously with the rate of Ag deposition up to broad plateau followed by a weak decrease. If, however, n_{Ag} exceeded about 10^{16} atoms $s^{-1} cm^{-2}$ (corresponding to a Ag concentration in the growing matrix of about 1%), the situation became unstable. An intense light flash accompanied by a sudden temperature rise, while the matrix became black indicating the formation of larger metallic particles.”

In contrast, cavity QED induced radiation depending on QED cavities in the condensing Ar liquid in the matrix and not the Ag clusters is consistent with these observations. If the cryogen cannot condense the Ar gas during the time the warmer Ag clusters are incoming, or if the concentration of Ar exceeds a certain limit, the temperature of the Ar rises. The light flash marking instability is likely caused because the increase in temperature momentarily increases the thermal kT energy of the Ar atoms, thereby producing greater suppressed IR and intense light emission.

Light Emission depends on Thermal kT Energy

“Finally, chemiluminescence is observed not only under the steady-state conditions of constant n_{Ag} , n_{Ar} , and T as discussed so far, but also if the deposition of n_{Ag} and n_{Ar} is interrupted and the matrix is subsequently warmed up, whereby the emitted intensity from the 10 K matrix is substantially larger than that from the 30 K sample.”

Since cavity QED induced light emission depends on suppressed IR that increases with warming from cryogenic temperature at 10 K, a substantially larger light intensity is expected upon warming. If the warm temperature T exceeds 30 K, the light intensity should be greater than that at 30 K by the ratio $T/30$.

Conclusions

The applicability of cavity QED induced EM radiation to the light emission from Ag cluster in a condensing Ar gas matrix requires analysis to show the 20 atom Ag clusters is indeed the largest that can produce light. The absorption coefficient α of argon at cryogenic temperatures is required to perform this analysis. Except for this, cavity QED induced EM radiation is consistent with the data for light emission from the Ag clusters in the growing matrix. In the pick-up experiment, light emission from bare Ag clusters is explained with QED induced radiation in QED cavities in the solid state that form in the Ag clusters as the Ar evaporates.

References

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