Low- and high-density features of IR luminescence of Xe₂ excimers produced by electron impact

A F Borghesani¹, G Carugno² and I Mogentale¹

¹ Department of Physics, University of Padua, Italy
² Istituto Nazionale di Fisica Nucleare, Sezione di Padova, via F Marzolo 8, I–35131 Padua, Italy

E-mail: borghesani@padova.infn.it

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Abstract

Electron-impact excitation of Xe atoms in pure Xe gas and in a Xe(10%)–Ar(90%) mixture has led to the discovery of infrared (IR) luminescence of Xe₂ excimers. The investigation of the emission spectrum at low density allows the identification of the molecular states involved in the transition. When the density is increased up to 40 times the density of the ideal gas at standard T and P, the interaction of the excimer with the dense environment produces a strong red-shift of the spectrum interpreted in terms of many-body effects.

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1. Introduction

The luminescence of rare gas (Rg) excimers is extensively studied for applications in vacuum ultraviolet (VUV) including the production of coherent and incoherent VUV light sources [1] and the detection of ionizing radiation [2]. Xe is of particular interest because of its efficiency to convert the excitation energy in intense VUV radiation. Upon excitation by means of several techniques including electrical discharges [3], irradiation with ionizing particles [4–6], or resonance lines [7–11], three-body collisions of excited and ground state atoms lead to the formation of the excited dimer, i.e., excimer, Xe₂⁺, whose decay from the lowest lying excited levels towards the dissociative ground state produces the 1st and 2nd VUV continua at about 152 and 170 nm.

Owing to their importance, these VUV excimer bands have been thoroughly studied theoretically [12–15] and experimentally [11, 16–19] to determine the molecular structure and potential energy curves and the kinetics of the deexcitation processes leading to the population of the 6s excited atomic states that are involved in the production of these molecular states [1, 8, 20–28].

At low pressure (P < 20 kPa), the VUV luminescence consists of the 1st continuum, whereas for higher P (>50 kPa), only the 2nd continuum is detected. This different pressure dependence has been explained by time-resolved spectroscopic studies showing that the 1st continuum is due to radiative transitions from the vibrationally excited (00')v’≥0 state correlated with the resonant 6s(3P₁) atomic state towards the dissociative 0' ground state, whereas the 2nd continuum consists of the overlapping bound-free emission from the lowest vibrationally relaxed (00'−, 1a) states correlated with the metastable 6s(3P₂) limit.

Hardly any attention has been paid to the possibility that molecular infrared (IR) transitions may occur in the cascade of processes leading to the formation of the states radiating in the VUV. Only an IR spectrum centred about 800 nm has been observed and attributed to a 0'→0' (6s[3/2]₁) → 0'→0' (6s[3/2]₀) transition [9]. One possible reason for this lack of interest in IR processes may be that the potential energy minimum of higher-lying excimer states occurs at an internuclear distance at which the weakly bound molecular ground state is strongly repulsive and is therefore not so easily accessible by multiphoton selective excitation. On the contrary, broad-band excitation techniques using high-energy charged particles [6, 21] may produce excited atoms of such high kinetic energy to collide with ground state atoms at short distance yielding molecular states in higher energy levels though their parity cannot be controlled.

We recently discovered a band in the near IR region centred at wavenumber νₚ ≈ 7800 cm⁻¹ [29]. Emission is produced by exciting the gas at room temperature with short pulses of 70 keV electrons. Details are found in the literature [29, 30]. This band occurs both in the pure gas...
and in an Ar (90%)–Xe (10%) mixture and is quite broad. At \( P \approx 20 \text{kPa} \), its FWHM (full width at half maximum) is \( \Gamma \approx 900 \text{ cm}^{-1} \). Its relative width \( \Gamma / \nu_m \approx 0.115 \) is comparable with that of the 2nd continuum \([5, 31]\). As the spectrum features in both gases at low \( P \) are identical, we attribute the emission to a Xe\(_2\) bound-free transition.

Improvements in our apparatus have allowed more accurate time-integrated measurements of the IR emission at low \( P \) and in an extended density range up to \( N \approx 8 \times 10^{26} \text{ m}^{-3} \), nearly 40 times larger than the density of the ideal gas at standard \( T \) and \( P \) (273 K and 0.1 MPa). By so doing, we now have the opportunity to better assign the molecular states involved in the transition and to elucidate the interaction of the excited molecules with a dense gas environment.

The electronic structure of homonuclear Rg excimers can be described by an ionic molecular core surrounded by an electron in a diffuse Rydberg orbital much larger in diameter than the internuclear distance \([12, 32, 33]\). Such a state can exist in a high-\( P \) environment provided that the optically active electron is only weakly scattered off the atoms of the host gas. This occurs if the electron mean free path is larger than the orbit of the Rydberg state as happens at low \( N \). It is therefore interesting to look at the evolution of a molecular Rydberg state when the environment becomes increasingly denser. In our previous experiments \([29, 30]\) we have mainly detected a red-shift of the IR emission spectrum of the excimer. In this experiment we confirm the previous results in an extended density range.

### 2. Low-density results

In figure 1 we show an experimental IR emission spectrum recorded in pure Xe gas at \( P \approx 0.1 \text{ MPa} \) at room temperature in an extended \( \tilde{\nu} \) range with 16 cm\(^{-1}\) resolution. The broad line is the molecular excimer band centred at \( \tilde{\nu}_m \approx 7800 \text{ cm}^{-1} \). Several atomic lines appear in the spectrum as expected because of the broad band excitation induced by electron impact. In particular, an atomic line due to a \( 7s[1/2]^0 \rightarrow 6p[1/2]_u \) atomic transition \([34]\) appears embedded in the excimer band. The closeness of such an atomic transition to the excimer spectrum suggests that the upper molecular state may be correlated with a 6p atomic limit.

Only recently theoretical potential energy curves for the higher lying Xe\(_2\) states have appeared in the literature \([14, 15]\). Thus, it is now possible to test the accuracy of some of the theoretical potentials by comparing this first experimental excimer IR emission spectrum with that simulated by using Franck–Condon calculations \([35, 36]\).

We assume that a bound-free transition is responsible for the IR emission and that the upper bound state is correlated with the \( 6p[1/2]_u \) atomic state. The molecular potential correlated with this state shows an avoided crossing with the \( g \) molecular state related to the \( 5d[1/2]_u \) state leading to predissociation \([23]\). The predissociation lifetime is estimated to be \( \tau_p \approx 10^{-10} \text{ s} \), whereas the mean time between collisions at the lowest density of this experiment, \( N_c \approx 2.4 \times 10^{25} \text{ m}^{-3} \), is \( \tau_c \approx 10^{-11} \text{ s} \). Thus, the large collision rate electronically stabilizes excimers before they predissociate.

At present, there are no estimates of the radiative lifetime and of the decay rate for vibrational relaxation for this bound state. We thus assume that they are not too different from those of the states responsible for the emission of the VUV continua. The radiative lifetimes of the highly excited vibrational states of the \( 0_u^+ \) and \((1_u, 0_u^-)\) molecular states correlated with the 6s atomic limit are estimated to be \( \tau_1 \approx 5 \text{ ns} \) \([20]\) and \( \tau_2 \approx 40 \text{ ns} \) \([16]\), respectively. Similarly, the decay rate for vibrational relaxation \( \kappa_3 \) is the same for all those states \([8]\), yielding a decay time \( \tau_3 = (\kappa_3 N_c)^{-1} \approx 0.65 \text{ ns} \).

This hierarchy of characteristic times supports the assumption that collisions stabilize excimers electronically and quickly establish thermal equilibrium among their internal rovibrational degrees of freedom.

Franck–Condon calculations require the knowledge of the potential energy curves whose choice among those reported in the literature \([15]\) has to meet several requirements: (i) the upper bound state must belong to the \( 6p \) atomic manifold; (ii) the parity of initial and final states must obey the selection rules \( u \leftrightarrow g \) and \( ' \leftrightarrow ^{\prime} \); (iii) the energy difference between the two potentials at the coordinate of the minimum of the bound state must be nearly equal to the central wavenumber \( \tilde{\nu}_m \) of the spectrum.

Accordingly, the upper bound state has been assigned as the \((3)0_u^+\) undergarde state correlated with the \( 6p(1D_2) \) limit (with some contributions due to the mixing with a 5d atomic state) \([15]\). The lower dissociative state has been assigned as the \((1)0_u^{-}\) gerade state correlated with the \( 6s(1P_1) \) resonant atomic state \([15]\). For both of these molecular states the projection \( \Omega \) of the electronic angular momentum along the molecular axis is zero. Thus, as in this transition \( \Omega = 0 \rightarrow \Omega = 0 \), the selection rule for the total molecular angular momentum \( \Delta J = \pm 1 \) must also be taken into account.

The intensity of the line shape, at infinite resolution, is computed within the centroid approximation because the electronic transition moments are not known as a function of the internuclear coordinates for the states at hand \([35, 36]\), thus yielding

\[
I (\tilde{\nu}) \propto \sum_{\nu J} e^{-\beta E_{\nu J}} \tilde{\nu}^4 \left\{ (J' + 1) |(\epsilon'', J' + 1 | \nu', J')|^2 \\
+ J' |(\epsilon'', J' - 1 | \nu', J')|^2 \right\} 
\]

(1)
where the selection rule $J' - J'' = \pm 1$ is enforced. As usual, a prime refers to the initial state (the bound one, in this case) and a double prime refers to the final state [35]. $E_{\nu',J'}$ is the energy of a rovibrational level of the bound state and is given by

$$E_{\nu',J'} = D_{e}^{\prime} \left[ 1 + \epsilon_{\nu} \right] + B_{e}^{\prime} J^{\prime} \left( J^{\prime} + 1 \right)$$

(2)

where $D_{e}^{\prime}$ is the dissociation energy of the upper state and $\epsilon_{\nu}$ are the dimensionless vibrational eigenvalues measured from the dissociation limit. $B_{e}^{\prime} = \hbar^2 / 2m_{e} R_{e}$ is the rotational constant. $m_{e}$ is the Xe\textsubscript{2} reduced mass and $R_{e}$ is the equilibrium internuclear distance of the bound state. The energy of the emitted photon is

$$\hat{\nu} = \left[ T_{e}^{\prime} - T_{e}^{\prime\prime} - D_{e}^{\prime} + E_{\nu',J'} - \epsilon_{\nu} \right]$$

(3)

in which $T_{e}^{\prime}$ and $T_{e}^{\prime\prime}$ are the values of the potential energy curve minima of the two states. $D_{e}^{\prime}$ and $D_{e}^{\prime\prime}$ are the well depths. The $0^{\prime\prime}_{g}$ state, though mainly dissociative, has a small attractive well at large internuclear distance with minimum at $R_{e}^{\prime\prime}$.

$|\nu', J\rangle$ is the eigenfunction of a rovibrational state of the bound potential. $|\nu'', J\rangle$ is a scattering state of kinetic energy $\epsilon_{\nu}^{\prime\prime}$ and total angular momentum $J''$ in the vibrational continuum of the dissociative potential. The Boltzmann factor $\exp(-\beta e_{\nu,J'})$ in equation (1) accounts for the equilibrium thermal distribution of the vibrational degrees of freedom with $\beta^{-1} = k_{B} T \approx 208.5 \text{ cm}^{-1}$ at room temperature.

$e_{\nu}^{\prime}$ and $|\nu', J\rangle$ are found by numerically integrating the Schrödinger equation for the rotationless potential of the bound state by adopting the Numerov–Cooley finite difference scheme [37] and replacing the centrifugal potential with the constant value $B_{e}^{\prime} J^{\prime} (J^{\prime} + 1)$ [38]. For numerical purposes, the literature $0^{\prime}_{g}$ potential has been accurately fitted to a Morse potential

$$V_{0^{\prime}_{g}} (R) = T_{e}^{\prime} + D_{e}^{\prime} \left[ 1 - e^{-[\beta_{e} (R - R_{e})]} \right]^2$$

(4)

with $T_{e}^{\prime} = 13860 \text{ cm}^{-1}$, $D_{e}^{\prime} = 1717 \text{ cm}^{-1}$, $R_{e} = 3.23 \text{ Å}$, and $\beta_{e} R_{e} = 6.734$. The bound state accommodates approximately 34 vibrational states though only the first few contribute significantly to the spectrum because of the Boltzmann factor.

The rotational constant is quite small $B_{e}^{\prime} \approx 2.47 \times 10^{-2} \text{ cm}^{-1}$, corresponding to a rotational temperature $T_{0} \approx 3.5 \times 10^{-2} \text{ K}$. Thus, the thermal population of rotational states is non negligible up to $J' \approx 250$.

The scattering eigenfunctions of the dissociative potential $|\nu'', J''\rangle$ are found by numerically integrating the Schrödinger equation with the effective potential

$$V_{i} = V_{0^{\prime}_{g}} (R) + \frac{\hbar^2}{2m_{e} R_{e}^2} J^{''} (J^{''} + 1)$$

(5)

in which $V_{0^{\prime}_{g}} (R)$ is the rotationless potential of the dissociative state, characterized by a well depth $D_{e}^{''} \approx 218 \text{ cm}^{-1}$ at $R_{e} \approx 4.92 \text{ Å}$ and by $T_{e}^{''} \approx 4779 \text{ cm}^{-1}$ [15]. For numerical purposes, the potential is cast in the form

$$V_{0^{\prime}_{g}} (R) = T_{e}^{''} + D_{e}^{''} f (x)$$

in which $f (x)$ is an analytical HFD–B potential [39] and $x = R / R_{e}$. A Runge–Kutta 4th order integration scheme with adaptive stepsize control is used [40]. The scattering wave functions are normalized to unitary incoming flux [41]

$$\psi_{\nu} \equiv \langle R | \nu'', J'' \rangle \rightarrow \frac{2 m_{e}}{\pi \hbar^2 k} \left( \frac{2 m_{e}}{\pi \hbar^2 k} \right)^{1/2} \sin (kR + \eta)$$

(6)

in which $k = [(2m_{e} / \hbar^2) \epsilon_{\nu}]^{1/2}$ is the wave vector and $\eta$ is the appropriate phaseshift.

The overlap integrals in equation (1) are evaluated by spline interpolation and quadrature [42] and the calculated spectrum is convoluted with the instrumental function to account for the finite resolution.

In figure 2, we compare the experimental and calculated spectra. The dashed line is the spectrum calculated by using the theoretical potential energy curves found in the literature. The agreement is only qualitative. The synthetic spectrum is centred at much smaller wavenumbers and its width is much larger than the experimental one. These features are the consequence of the fact that the theoretical potential energy curves are too close to each other and that the dissociative potential is probably too steep in the region of the minimum of the bound state. The only correct feature of the computed spectrum is its asymmetric shape with a longer tail towards higher energies that is due to the non negligible contribution of vibrational states with $\nu' > 0$.

It is, however, possible, by inverting the line shape, to reconstruct the repulsive part of the dissociative potential in a coordinate range, over which the vibrational wavefunctions of the bound state are non negligible [36]. As only a few vibrational levels of the bound state are thermally excited, the choice of the analytical form of the bound state potential is not too critical and we assume that it is correctly described by the theoretical literature potential (3) $0^{\prime}_{u}$ [15]. We also assume that the repulsive part of the potential of the dissociative (1) $0^{\prime\prime}_{u}$ state is described by an inverse power law potential of the type

$$V_{r} = T_{0} + V_{0}/x^{12} \quad (x = R / R_{e})$$

(7)

in which $T_{0}$ and $V_{0}$ are adjustable parameters. For each ($T_{0}$, $V_{0}$) pair, the scattering eigenfunctions are to be computed.
and is the central wavenumber of the spectrum, \( \nu = 4.0 \times 10^3 \) (8). The spectrum computed by using these values of the parameters is shown as a thick solid line in figure 2 and is in nearly perfect agreement with the experimental one. The blue asymmetry of the experimental spectrum is also well reproduced.

In figure 3 we compare the theoretical and best fit potentials. We also plot the potential energy curve of the upper bound state along with the vibrational eigenfunctions for \( \nu' = 0 \) and 8. The best agreement with the observed spectrum is obtained by setting \( T_0 = (5315 \pm 32) \text{ cm}^{-1} \) and \( V_0 = (760 \pm 16) \text{ cm}^{-1} \). The spectrum computed by using these values of the parameters is shown as a thick solid line in figure 2 and is in nearly perfect agreement with the experimental one. The blue asymmetry of the experimental spectrum is also well reproduced.

\[ \nu_m = \nu_{m,0} = AN \] (8)

describes accurately the experimental data.

This linear trend is observed both in pure Xe gas and in the mixture, though the slope has different values in the two cases, and is obeyed up to \( N \approx 8 \times 10^{20} \text{ m}^{-3} \approx 40N_{i,g} \), where \( N_{i,g} \) is the ideal gas density at \( T = 273 \text{ K} \) and \( P = 0.1 \text{ MPa} \).

In figure 4 the central wavenumber of the spectrum, \( \bar{\nu}_m \), is shown as a function of \( N \). In the limit \( N \to 0 \), \( \bar{\nu}_m \) has the same value as the Xe\(_2\) excimer being produced either in the pure gas or in the mixture. By contrast, when the Xe\(_2\) excimer is produced in the pure gas, the density dependence of \( \bar{\nu}_m \) is much stronger than in the case in which Xe\(_2\) is produced in the mixture. If the data are fit to straight lines, the following values for the slope are obtained: \( A = (2.08 \pm 0.04) \times 10^{-22} \text{ m}^2 \) in pure Xe and \( A = (0.63 \pm 0.015) \times 10^{-22} \text{ m}^2 \) in the mixture. We have to stress the fact, however, that the lines in figure 4 are not such linear fits but represent the prediction of a simple theoretical model we have developed [29].

According to Mulliken [12], an excited state of a diatomic Rg molecule can be envisaged as an ionic core, e.g. Xe\(_2\), plus a Rydberg electron in an extended orbital. We assume that the electron is so largely delocalized that many atoms of the host gas are encompassed within the large electron orbit and are polarized by the strong field of the ionic core. If \( N \) is large enough, we can assume that the dielectric screening exerted by the polarized atoms can be accounted for by the dielectric constant of the gas, \( K(N) \).

The interaction potentials are of electrostatic nature and are therefore reduced by a factor \( 1/K^2 \) with respect to the dilute gas condition. Thus, the energy difference between the upper bound potential \( V_{0+} \) and the lower dissociative potential \( V_{0-} \) is reduced by the same factor. At the densities of the experiment, \( K(N) \) can be Taylor-expanded to first order in \( N : K \approx 1 + N\alpha/\epsilon_0 \), where \( \alpha \) is the atomic polarizability of the atoms of the gas and \( \epsilon_0 \) is the vacuum permittivity.

The average energy difference that approximately corresponds to the central wavenumber of the observed emission spectrum is thus given by

\[ \bar{\nu}_m = \frac{(V_{0+} - V_{0-})}{hcK^2(N)} \approx \nu_{m,0} \left( 1 - \frac{2\alpha}{\epsilon_0}N \right) , \] (9)

in which \( \nu_{m,0} = (V_{0+} - V_{0-})/hc \) and \( \langle \cdots \rangle \) is a suitable weighted average of the potentials over the coordinates of the vibrational states of the bound potentials. \( \nu_{m,0} \) is the

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**Figure 3.** Comparison of the potential energy curves for the dissociative state \( 0^+ \). Thin solid line: literature potential [15]. Thick solid line: best fit potential. The bound state potential is shown with the eigenfunctions for \( \nu' = 0 \) and 8.

**Figure 4.** Density-dependent shift of the centre of the excimer emission spectrum. Open dots: pure Xe. Closed dots: Ar(90%)-Xe(10%) mixture. Lines: prediction of the theoretical model.
zero-density limit of the central wavenumber of the emission spectrum. A linear dependence of $\tilde{v}_m$ is thus obtained.

This contribution to the shift is due to the solvation of the excimer by the surrounding atoms. Unfortunately, this effect is not sufficient to describe the experimental results. In fact, its slope $\tilde{v}_{m,0}/\epsilon_0$ is approximately equal to only one half of the observed slope. We can thus conclude that there must be another physical mechanism producing a shift of the centre of the spectrum that is linear with the density. In this case, the resulting slope would add to that due to solvation.

The missing contribution arises from quantum many-body effects in the interaction of the delocalized electron with the atoms of the surrounding gas. In fact, the wavelength of the loosely bound Rydberg electron is very large and spans over many surrounding atoms. Such a state can exist provided the electron is weakly scattered off the gas atoms, i.e. if the mean free path is much larger than the radius of its orbit, as it occurs in the present case [29]. In this case, the Rydberg electron can be considered as nearly free and its simultaneous interaction with many atoms of the host gas leads to a density-dependent shift of its energy given by [43]

$$\Delta E(N) = \frac{2\pi \hbar^2}{m} N a$$

where $a$ is the electron–atom scattering length and $m$ is the electron mass.

This contribution has to be added to the energy difference between the initial and final state of the molecule, eventually leading to the following expression for the energy of the emitted IR photon in the centre of the spectrum

$$\tilde{v}_m = \tilde{v}_{m,0} \left( 1 - \frac{2\alpha}{\epsilon_0} N \right) + \frac{\hbar}{mc} N a = \tilde{v}_{m,0} - \left( \frac{2\alpha}{\epsilon_0} - \frac{\hbar a}{mc} \right) N.$$  \hspace{1cm} (11)

This model predicts a linear density-dependence of $\tilde{v}_m$, as actually observed. Moreover, the slope can be calculated if the gas parameters $\alpha$ and $a$ are known. In the case of the heavier Rgs, the scattering length is negative and its contribution effectively adds to the solvation contribution.

In the pure gas, the choice of the gas parameters is obvious. For the mixture, the low Xe concentration leads to the assumption that the excimer is actually surrounded by Ar atoms so that the Ar parameters have to be chosen. For pure Xe, $\alpha = 4.45 \times 10^{-45}$ F·m [44] and $a = -3.09$ Å [45], yielding $(2\tilde{v}_{m,0}/\epsilon_0 - \hbar a/mc) = 1.98 \times 10^{-22}$ m$^2$, to be compared with the experimental value $(2.08 \pm 0.04) \times 10^{-22}$ m$^2$. For the mixture, the Ar parameters are $\alpha = 1.827 \times 10^{-40}$ F·m [44] and $a = -0.86$ Å [45], yielding a slope $0.66 \times 10^{-22}$ m$^2$ to be compared with the experimental value $(0.63 \pm 0.015) \times 10^{-22}$ m$^2$.

The theoretical prediction agrees very well with the experiment. In figure 4 the straight lines actually represent the theoretical prediction and are not a mere linear fit to the data.

It is interesting to note that the dielectric screening effect always produces a red-shift of the excimer emission spectrum because it reduces the strength of the Coulomb interaction between the Rydberg electron and the ion core. On the contrary, the multiple scattering effect gives a contribution to the energy of the emitted photon whose sign depends on the nature of the (nearly free) electron–atom interaction. If this is attractive, as in the case of the heavier Rgs, the electron–atom scattering length is negative, whereas it is positive in the case of Ne and He. Thus, roughly speaking, the density-dependent shift of the emission spectrum might be ‘fine tuned’ from red- to (even) blue-shift by suitably choosing the buffer gas in which Xe excimers are produced. Further investigations in different mixtures should help confirming this model.

4. Conclusions

The study of the IR emission spectrum of Xe excimers in pure Xe gas or in an Ar–Xe mixture reveals interesting features in both the low- and high-density limits. The analysis of the spectrum at low density has allowed the assignment of the molecular states involved in the transition. This was never done before because no IR molecular spectra of Xe in the present range were observed previously. Moreover, it has been possible to give an experimental determination of the potential energy curve of a gerade molecular state related to the 6s manifold.

On the other hand, it has been possible to see how cooperative- and many-body effects continuously develop by increasing the density up to quite high values. The change of the excimer emission spectrum with the gas density reveals (at least) two kinds of mechanisms, one classical and one quantum, affect the interaction of the excimer with its environment. In our opinion, it is worth noting that the quantum contribution to the self-energy of the nearly free Rydberg electron links a typical issue of molecular physics such as the emission spectrum of a decaying diatomic molecule to the (apparently) uncorrelated realm of electron transport in dense gases. In fact, also in that case the density dependent shift of the electron energy due to multiple scattering deeply affects electron transport [46–48].

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