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Simulating the broad-band radiation of gas-discharge krypton-xenon plasma

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Abstract. Experimental broad-band continuum emitted by electric-discharge Kr+Xe plasma is interpreted as the KrXe* and Xe_2 molecules emission due to the $0^+(^3P_1) \rightarrow 0^+(^1S_0)$ bound-free transitions. Using the literature data for the $0^+(^3P_1)$ and the $0^+(^1S_0)$ internuclear potentials and a dipole moment function the relative intensities of the v, $0^+(^3P_1) \rightarrow \varepsilon$, $0^+(^1S_0)$ transitions were calculated in relation to the transition wavelengths. It is noted that internuclear potentials for the Xe_2 molecule used in the present work allowed one to describe the long-wavelength wing of experimental spectra under consideration quite adequately. As to the KrXe* model continuum which is associated with the short-wavelength region of the same spectra it proved to be shifted to short-wavelength side at 5–7 nm in comparison with experiment, and its width proved to be half of experimental one.

PACS. 33.20.Tp Vibrational analysis

1 Introduction

Emission spectra of Kr+Xe gas-discharge plasma were investigated recently in VUV diapason over a wide range of experimental conditions [1–3]. Capillary [1,2] and barrier discharges [3] were under investigation, host- and guest-gas pressure were varied, and discharge temperature was regulated with the cooling of the discharge capillary walls. The main result of these works lies in the fact that the KrXe* and Xe_2 molecules emission is responsible for the form of spectra under discussion. As to the homonuclear molecule Xe_2 its emission presents a well-known continuum [4,5] which is due to bound-free transitions from the vibrational levels of two lowest excited bound electronic states $0^+(^3P_1)$ and $1(^3P_2)$ of the Xe_2 molecule to the repulsive branch of its ground state $0^+(^1S_0)$.

As to the heteronuclear molecule KrXe* its emission was found to be concentrated over a narrow spectral interval in the neighbourhood of the Xe atom resonance line (∼148 nm) at general pressure of a mixture around 10–100 hPa, and as pressure was increased till 200–400 hPa comparatively broad continuum at 150–160 nm appeared in addition to above-mentioned narrow band.

From an application standpoint a narrow-band emission of the KrXe* molecule was of principal interest to the authors of experimental works [1–3] cited above. This interest centres around possibility to ‘pump’ discharge energy into narrow-band emission and to get lasing. Narrow-band emission was interpreted in detail in reference [6].

The aim of the present work is to simulate broad long-wavelength continuum in the KrXe* molecule spectrum. The present work was stimulated firstly by the availability of experimental spectra [1–3] observed for different types of discharge and at different parameters of discharge. It is worth noting that spectrum holds its structure in spite of the variety of experimental conditions. Besides the potential curves for the KrXe* molecule electronic states presumably taking part in forming spectrum under consideration were published recently [7]. Therefore the procedure which we developed earlier [8] to interpret experimental spectra of the homonuclear molecules Kr_2 and Xe_2 may be applied here to interpret the KrXe* molecule continuum. We emphasize also that the curves [7] were calculated ab initio, so any comparison with experiment will be very useful for estimating the reliability of the calculational procedure.

2 Statement of the problem

Under assumption that the KrXe* molecule spectrum is determined by the dipole transitions to the ground state $0^+(^1S_0)$ from the excited states dissociated into atomic states $Kr(4p^6\ ^1S_0)$ + Xe $(5p^56s\ ^3P_1,\ ^3P_2)$ that excited states should be considered which have nonzero transition matrix elements. Three electronic states of this kind are known: $0^+(^3P_1)$ dissociated into $Kr(4p^6\ ^1S_0)$ + $Xe(5p^56s\ ^3P_1)$, $1(^3P_1)$ dissociated into the same atomic states, and $1(^3P_2)$ dissociated into $Kr(4p^6\ ^1S_0)$ + $Xe(5p^56s\ ^3P_2)$. The potential curves [7] for excited states $0^+(^3P_1)$, $1(^3P_2)$, and ground state $0^+(^1S_0)$ (dissociated

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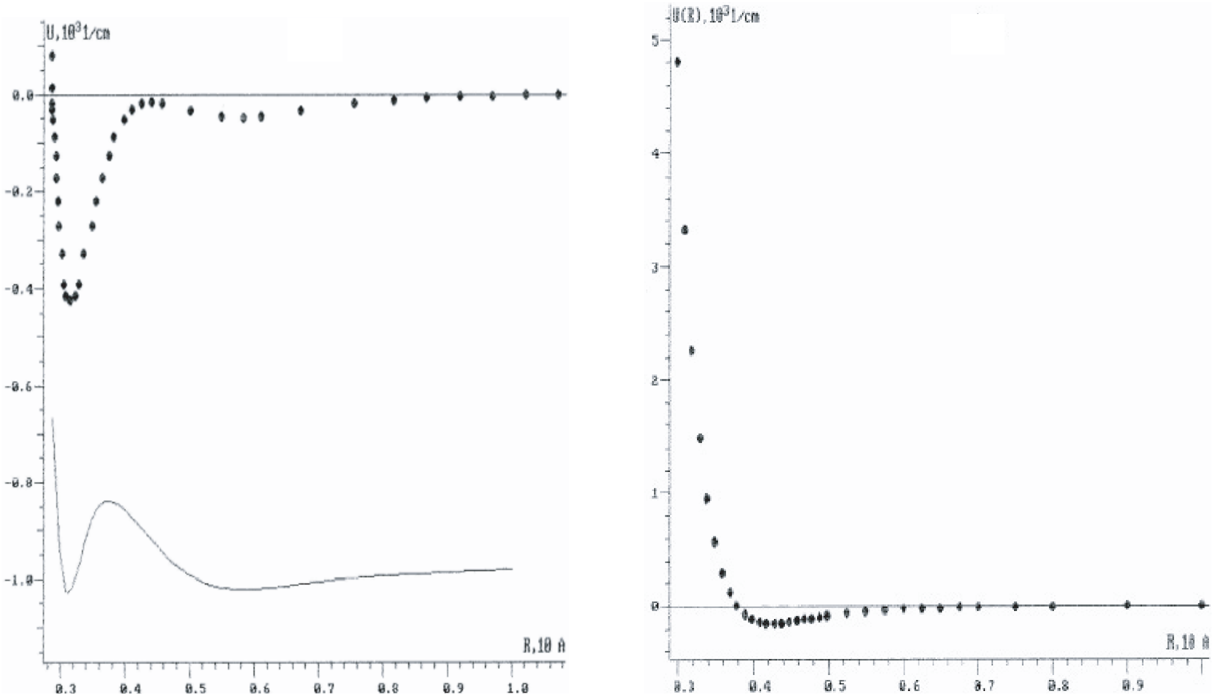


(a) (b)

Fig. 1. The KrXe* molecule potential curves (from Ref. [7]): (a) $0^+(^3\mathrm{P}_1)$ (●), $1(^3\mathrm{P}_2)$ (——), the Xe($5p^5 6s\ ^3\mathrm{P}_1$) atomic level is accepted as zero; (b) $0^+(^1\mathrm{S}_0)$, the Xe($5p^6\ ^1\mathrm{S}_0$) atomic level is accepted as zero.

into atomic states Kr($4p^6\ ^1\mathrm{S}_0$) + Xe($5p^6\ ^1\mathrm{S}_0$)) are presented in Figure 1. As to the state $1(^3\mathrm{P}_1)$ we eliminate it from consideration for reason to be presented below.

The curve $0^+(^3\mathrm{P}_1)$ has two minima — inner and outer. These minima are situated at the internuclear distance $R = 3.160$ and 5.736 Å, and their depths are 423 and 49 cm^{-1} respectively. The curve $1(^3\mathrm{P}_2)$ is a double-well curve also, inner and outer wells are situated at $R = 3.116$ and 5.760 Å, and their depths are equal to 51 and 45 cm^{-1} respectively, and the barrier between minima is of a height 140 cm^{-1} at $R = 3.741$ Å. The curve $0^+(^1\mathrm{S}_0)$ shows single minimum of a depth 153 cm^{-1} at $R = 4.239$ Å. When solving the vibrational equation with the potential $0^+(^3\mathrm{P}_1)$ it was shown in [7] (and in present work also) that the lower vibrational states ($v = 0$–7) are localized in the inner well, and the differences of their energies are the following: $E_{v=7} - E_{v=6} \sim 36$ cm^{-1}, $E_{v=1} - E_{v=0} \sim 63$ cm^{-1}. The states with $v = 8$–10, 12–15 are localized in the outer well and $E_{v=9} - E_{v=8} \sim 5.5$ cm^{-1}. So the 'inner' vibrational quantum is nearly an order of magnitude more than the 'outer' one. Taking this relation into account one may suppose that at high general pressure of the Kr + Xe mixture a collisional relaxation goes along the vibrational levels both of the outer and the inner wells. Correspondingly the KrXe* molecule emits from the bottom both of the outer ($\lambda \sim 148$ nm) and the inner ($\lambda \sim 153$ nm) wells. As general pressure decreases relaxation proceeds predominantly along that channel where the vibrational quantum are less, that is along the vibrational levels of the outer well. So as pressure decreases molecule emits from the bottom of the outer well at a wavelength ~148 nm. Referring to Figure 1 it is easy to see that transitions from the inner well of the $0^+(^3\mathrm{P}_1)$ curve come to the repulsive branch of the ground state $0^+(^1\mathrm{S}_0)$ forming continuum at ~153 nm. At the same time transitions from the outer well of the $0^+(^3\mathrm{P}_1)$ curve fall on the bound vibration levels of the $0^+(^1\mathrm{S}_0)$ curve forming quasi-continuous narrow band at 148 nm. Much the same could be told about transitions from the state $1(^3\mathrm{P}_2)$ as the inner and outer minima of the corresponding potential curve are situated nearly at the same internuclear distances as minima of the $0^+(^3\mathrm{P}_1)$ curve are (Fig. 1). However when solving the vibrational equation with the $1(^3\mathrm{P}_2)$ potential it occurred that the vibrational levels $v = 0$–5 were localized in the outer well. Thus it may be concluded that transitions from the state $1(^3\mathrm{P}_2)$ come from the outer well bottom and hereby their contribution to broad-band continuum may be neglected.

As to the $1(^3\mathrm{P}_1)$ curve which is not displayed in Figure 1 it should be pointed out that according reference [7] this curve has single minimum at $R = 5.896$ Å with the depth of 45 cm^{-1}. Internuclear distance wherein potential is zero is equal 4.858 Å. Therefore it can be concluded that transitions from this state contribute significantly only to narrow-band emission at ~148 cm^{-1}.

Hence the bound-free transitions

$$v, 0^+(^3P_1) \rightarrow \varepsilon, 0^+(^1S_0),$$

going on with participation of the lower vibrational states localized in the inner well of the $0^+(^3\mathrm{P}_1)$ curve should be considered for interpreting the KrXe* broad-band continuum. Remind that these states have $v = 0$–7.

3 The simulation of experimental spectrum

For better understanding of the following presentation recall briefly a procedure of reference [8]. It is based on a numerical calculation of the relative density of the energy distribution $I_v(\lambda)$ radiated due to the bound-free transition $v \to \varepsilon$ from the vibrational level v of the bound electronic state to the repulsive electronic state at a certain positive energy value ε. Having got a set of the functions $I_v(\lambda)$ for different values of a vibrational quantum number v we approximate experimental spectrum $I(\lambda)$ as an expansion

$$I(\lambda) = \Sigma_v C_v I_v(\lambda). \tag{1}$$

The weight coefficients C_v are found with the least-squares method using the code BARSIC [9], and we interpret them as relative populations of the vibrational levels v. The functions $I_v(\lambda)$ are described with an accuracy of constant by the following equation [10]:

$$I_v(\lambda) = \varepsilon^{-1/2}\lambda^{-6}|\textstyle\int \psi_v(R)\mu(R)\psi_\varepsilon(R)dR|^2. \tag{2}$$

Here λ is the wavelength of the $v \to \varepsilon$ bound-free transition, $\psi_v(R)$ is a vibrational wavefunction of the level v of the upper bound state $0^+(^3\mathrm{P}_1)$, $\mu(R)$ is the dipole moment function of the transition $0^+(^3\mathrm{P}_1) \to 0^+(^1\mathrm{S}_0)$ [7], $\psi_\varepsilon(R)$ is a vibrational wavefunction of the lower repulsive state $0^+(^1\mathrm{S}_0)$ corresponding to the positive energy value ε. An amplitude of a function $\psi_\varepsilon(R)$ is normalized at large R to the value of $\pi^{-1/2}\varepsilon^{-1/4}$. The wavefunctions are found by numerical integration of the vibrational Schrödinger equation

$$d^2\psi/dR^2 + [E - U(R)]\psi = 0 \tag{3}$$

by the Numerov method in the modification of reference [11]. Internuclear potentials $U(R)$ both of the upper and the lower electronic states were taken from reference [7].

It is evident that the foregoing is based upon the assumption that experimental spectrum may be described with transitions from a single excited electronic states. This assumption was justified in the preceding section.

4 The Xe$_2$ molecule contribution

The above-mentioned procedure could be realized with the functions $I_v(\lambda)$ derived only for the KrXe* molecule if there were not a contribution of emission of a molecule Xe$_2$ to experimental spectra [1–3] which should be considered as a function $I(\lambda)$ in equation (1). As there is no way to separate a priori the contributions of the KrXe* and Xe$_2$ molecules to spectra under discussion we added to expansion (1) the functions $I_v(\lambda)$ which were obtained by us earlier in reference [8]. Remind that in reference [8] we have interpreted spectra of gas-discharge plasma in pure xenon as a result of the bound-free transitions v, $0^+(^3\mathrm{P}_1) \to \varepsilon$, $0^+(^1\mathrm{S}_0)$ in a molecule Xe$_2$. The functions $I_v(\lambda)$ were calculated in reference [8] with a procedure presented in the preceding section using potentials $0^+(^3\mathrm{P}_1)$ [12], $0^+(^1\mathrm{S}_0)$ [13], and the dipole moment function was approximated as a constant.

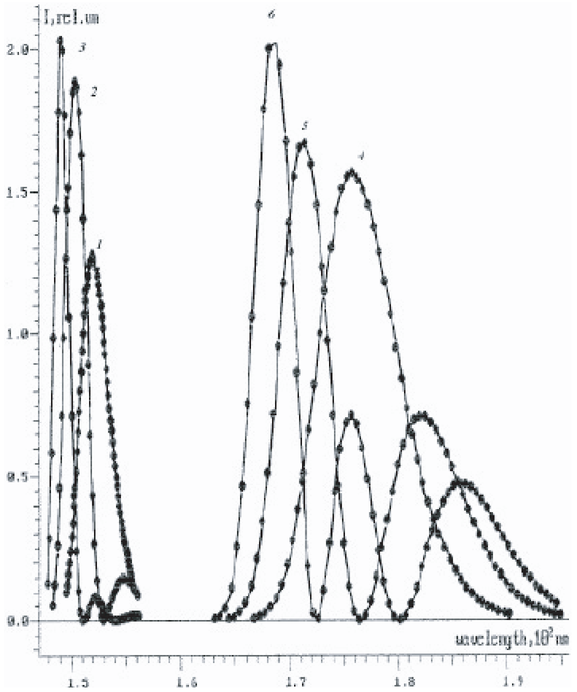
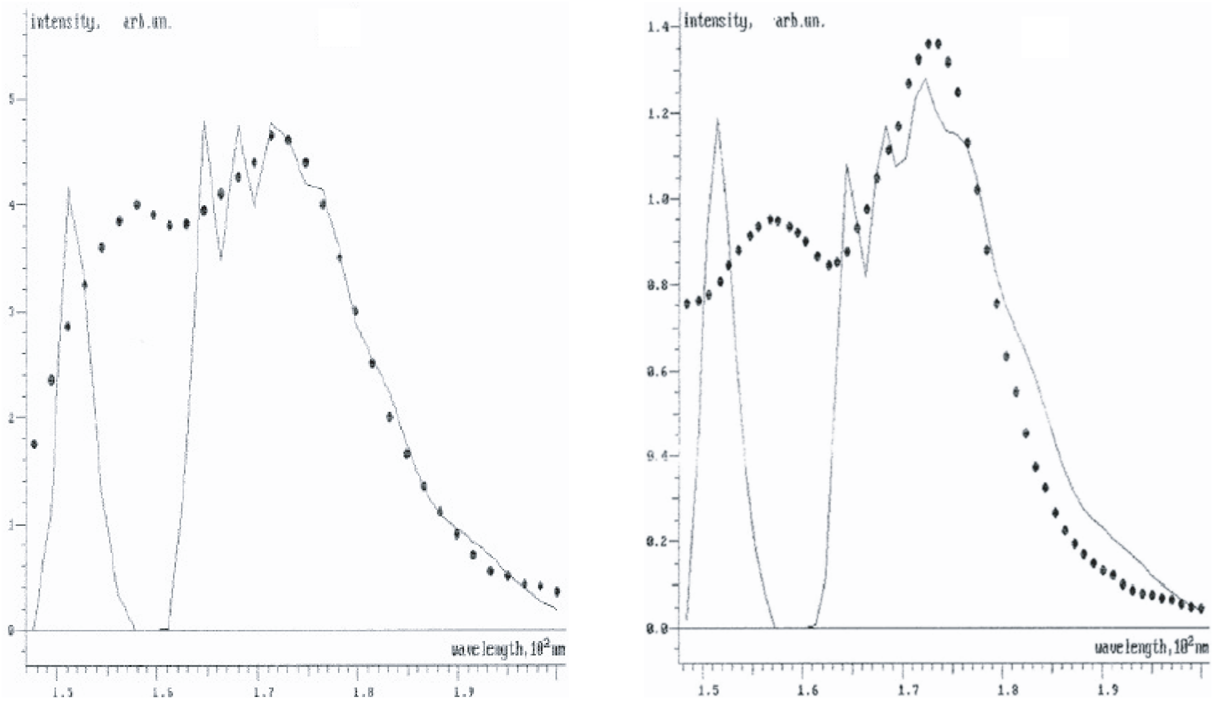


Fig. 2. The $I_v(\lambda)$ curves calculated with equation (2) for the KrXe* (*1–3*) and Xe$_2$ (*4–6*) molecules: $v = 0$ (*1, 4*), 1 (*2, 5*), 2 (*3, 6*).

5 Results and discussion

The functions $I_v(\lambda)$ both for the KrXe* and Xe$_2$ molecules are presented in Figure 2. It is obvious that the functions $I_v(\lambda)$ describing the contributions of different molecules to observed spectrum should be involved in expansion (1) with the coefficients depending on the molecules concentration and populations of the corresponding states. However the present case is simplified as the KrXe* and Xe$_2$ functions $I_v(\lambda)$ are not overlapping (Fig. 2). Roughly speaking according the present calculations the molecule KrXe* cut off its emission (on a wavelength scale) whereas the molecule Xe$_2$ does not yet begin to emit. At the same time it means that the modelled KrXe*+Xe$_2$ spectrum will show a crevase at ~160 nm. This crevase may be assigned in part to the fact that the short-wavelength wing of Xe$_2$ continuum (the so-called first continuum [4,5]) is ill fitted [8] with the functions $I_v(\lambda)$ from Figure 2, but simultaneously this crevase means that it would be good to shift the rated KrXe* spectrum to the long-wavelength region at 5–7 nm. The latter could be accomplished with the corresponding correction of the potential curves $0^+(^3\mathrm{P}_1)$, $0^+(^1\mathrm{S}_0)$ shown in Figure 1, and this conclusion may be considered as the first result of comparing reference [7] with experiment.

In present work spectrum of a barrier discharge [3] in the Kr+Xe mixture (general pressure is 400 hPa, admixture of Xe is 1%) and capillary-discharge spectrum derived at the same conditions were taken as the functions $I(\lambda)$. The coefficients C_v of the expansion (1) were obtained with the aid of the BARSIC code [9].



(a) (b)

Fig. 3. Experimental (dotted lines) and model (solid lines) spectra of electric-discharge plasma of the Kr+Xe mixture: (a) a barrier discharge, (b) a capillary discharge.

Model spectra (solid lines) and experimental ones (dotted lines) are compared in Figure 3.

Experimental maxima at 157 and 173 nm are assigned commonly to the KrXe* broad-band continuum and to so-called Xe$_2$ second continuum respectively. It is easy to see that long-wavelength wing of experimental spectra is approximated quite adequately, and this circumstance confirms both the good quality of the internuclear potentials [12,13] and interpretation of long-wavelength wing as the Xe$_2$ molecule emission. On contrary the short-wavelength wing is approximated much worse. The gap which a model curve shows at 157–160 nm was discussed above. Besides it is clear that a mere shift of the KrXe* model spectrum to the long-wavelength side would be insufficient to get a good agreement with experimental spectrum as a width of the KrXe* model spectrum (5–6 nm) is nearly half of experimental one. A possible way of broadening the KrXe* model continuum is to increase a steepness of a repulsive branch of the $0^+(^1S_0)$ potential from reference [7]. Note to the point that an increase of a steepness of a repulsive branch will result simultaneously in shifting the model spectra to the long-wavelength region as the interval between the lower and the upper potential curves decreases (Fig. 1). In our opinion this way of correcting the KrXe* potential $0^+(^1S_0)$ [7] is worth of attempt.

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