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Rempi and LRF spectroscopy of Kr_2^* excimer

M. HEMICI, R. SAOUDI, E. DESCROIX, E. AUDOUARD and P. LAPORTE

Laboratoire Traitement du Signal et Instrumentation (T.S.I.), URA 842 du CNRS, Université Jean Monet, Faculté des Sciences et Techniques, 23 rue du Dr Paul Michelon, 42023 Saint-Etienne cedex 2, France

Rare gases have attracted considerable attention since a long time in both fondamental and applied research. Spectroscopy and kinetics have been investigated in details particularly the excimer formation and decay [1]. In particular recent progress in the short distance relaxed excimer spectroscopy have been performed as well from the experimental point of view [2-5] as from the theoretical one with the improvement of the *ab initio* calculation accuracy [6]. Meaningful comparisons are therefore now quite realistic.

In the present work we report on the molecular spectroscopy associated with upper state transitions from the relaxed $^3\Sigma_u^+$ (3P_2) krypton excimer state using timely and spectrally resolved laser reduced fluorescence (LRF techniques). Such an approach which, to our best knowledge, has not been applied to this experimental situation appears to be a promising and powerful technique.

Wavelength dependent laser reduced fluorescence of the VUV excimer fluorescence at 145 nm (Fig. 1) is performed giving molecular spectra as illustrated in Fig. 2. The first step VUV selective excitation is obtained by a monochromatized laser plasma source [7], whereas the second step is performed using a tunable pulsed dye laser pumped by a YAG laser (10ns) equipped with harmonic generation. The tunable time delay between the two beams is performed with a nanosecond accuracy.

Fig.1 : Kr_2^* excimer emission versus time
Krypton pressure : 520 hPa; $\Delta t = 170$ ns
A : VUV excitation only,
B : VUV excitation and laser excitation at 499.4 nm illustrating the LRF phenomena

The experimental cell is also equipped with electrodes coupled to a very low current measurement capability circuit as previously described [3].

It is observed that very fast upper state dissociations occur giving possibly rise to subsequent two-photon ionization from the transient atomic species within the second laser pulse timewidth. REMPI spectra in the most general sense of multicolor, sequential, resonantly enhanced multiphoton ionization are observed as illustrated in Fig. 3. These combined LRF and REMPI techniques are a powerful experimental tool for detailed comparison with *ab initio* molecular potential calculations [6].

Fig.2 : LRF spectra (Krypton pressure : 400 hPa; $\Delta t = 380$ ns)

Fig.3 : REMPI spectra (Krypton pressure : 400 hPa; $\Delta t = 380$ ns)

In this work we shall restrict to the wavelength range corresponding to the C500 dye *i.e.* 485-550 nm. Actually apart from the infrared range [5,8] which is more complicated to experimentally investigate, this range corresponds to the second group of possible bound-bound transitions in an energy range for which *ab initio* calculations may be expected to remain enough accurate. This would be no longer the case if higher energy excited states were involved.

In addition even the most recently reported work do not exhibit a detailed experimental agreement, and safe assignments remain difficult.

Figure 2 displays clearly two groups of lines: a rather simple system (group I) around 500 nm and a much more complex and broad structure (group II) around 530 nm [corresponding to the superimposition of a broad continuum (bound free transitions) and of a discrete spectrum (bound-bound transitions)].

A detailed and unambiguous assignment of group II lines spectra is beyond the scope of these preliminary results. Indeed it has to be pointed out that the features exhibited in Fig. 2 are reproducible so that the spectrum appears rather congested. At this stage it may be remarked that such a situation is not surprising since these transitions may be ascribed to ${}^3\Sigma_g^+ \leftarrow {}^3\Sigma_u^+$ transition, according to *ab initio* calculations which have allowed a correct assignment of previously reported work.

Three states (VI)Og⁺, (V)Og⁻ and (VIII) 1_g, according to the labeling of Ref. [6], which have (3) ${}^{3,1}\Sigma_g^+$ parents are indeed very different of those with ${}^{3,1}\Pi_g$ parents. They have $[{}^2\Sigma_u^+]\sigma_u6p$ electronic character at short distance which transforms slowly into $[{}^2\Sigma_u^+]\sigma_g5p$ character at long distance. This electronic situation gives to these states the form of relatively shallow wells followed by a barrier to dissociation. The states with ${}^{3,1}\Pi_g$ parents have in contrast the same $[{}^2\Sigma_u^+]\pi_u6p$ character in the whole internuclear distance range and have only a strongly localized crossing with dissociative states. Thus the shape of absorption spectra is expected to be very different in each case as outlined above.

In agreement with the *ab initio* calculations [6] and with the most recent observation [5] group I may be ascribed to ${}^3\Pi_g \leftarrow {}^3\Sigma_u^+$ transitions. Indeed in the most recent calculations there are five states (VI)Og⁻, (VII)Og⁺, (IX)1_g, (X)1_g and (V)2_g after spin orbit coupling for the same (3) ${}^{3,1}\Pi_g$ parents. Yet all these states have the nature explained above and show a deep well with an equilibrium distance nearly the same as the one of ${}^3\Sigma_u^+(1_u0_u^-)$ state *i.e.* 5.22 bohr $\approx$ 2.761 Å. It has to be noticed that according to calculations all these states have also nearly the same value of ω_e (170 cm⁻¹) [6]. A calculation of the Franck Condon factors allows a direct comparison of experimental structures and theoretical predictions. In the calculations reported in Fig. 4 a fixed transition moment is assumed and a difference of 0.1 bohr (0.053 Å) between the lower and the upper state is taken into account. Due to systematic errors [6] the calculated transitions have to be shifted by a fixed value of 830 cm⁻¹ to be compared with the experiment. The satisfactory agreement between the experimental and theoretical features strongly supports the reported assignment

Fig.4 : comparison of experimental LRF spectra with Franck Condon factors calculation for $(V)2g^3\Pi_g \leftarrow (I)1u^3\Sigma_u^+$ transition ($v = 0,1,2$)

A detailed analysis of the three main bands of group I reveals a double peak structure in agreement with Eden and Coll. [5]. Despite the accuracy of our measurement which can be performed down to 200 mbar the additional small peaks reported by Langhoff and Coll. [4] are not observed. Such a structure can be attributed to either a vibrational structure of the same electronic transition as assumed in Fig. 4 or to different electronic transitions (involving several of the five relevant states). A detailed analysis taking into account the calculated transitions moments is thus requested. Such a work is still in progress.

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