PHYSICAL REVIEW A VOLUME 51, NUMBER 4 APRIL 1995

# Fine structure in krypton excimer

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(Received 17 November 1994)

By using laser reduced fluorescence techniques, molecular absorption from the first relaxed excited excimer states of krypton is obtained in the 960–990-nm wavelength range. Five bands are observed and analyzed by comparison with an *ab initio* calculated spectrum. The fine structure is thus evidenced.

PACS number(s): 33.20.Ea, 33.40.–e, 33.80.Rv, 33.70.Ca

In the past, important experimental effort has been aimed at obtaining the rare-gas infrared spectra associated with the relaxed excimer absorption [1–3]. During the past few years, important progress has been made in the understanding of excimer molecular structures at short internuclear distances through both new experimental approaches [4,5] and *ab initio* calculations [6]. It is the purpose of the present work to offer information on this challenging question, by providing a comparison between experimental spectra and calculated spectra using *ab initio* transition moment calculations. The infrared wavelength range is well suited for clear evidence of a spin-orbit coupling effect since the calculations predict a significant splitting between electronic states ($>20\ \mathrm{cm}^{-1}$) in the corresponding energy range. The highly excited excimer states are known to have a predissociative nature. Nevertheless, laser reduced fluorescence (LRF) techniques allow one to obtain molecular spectra independently of the upper excited-state nature [7]. Bound-bound transitions are mainly associated with absorptions from the ${}^3\Sigma_u^+(1_u,0_u^-)$ state towards excimer states with ${}^{3,1}\Pi_g$ parentage. Such molecular absorption in the 955–995-nm range is analyzed in detail in the present work.

One-photon vacuum ultraviolet (vuv) selective excitation of the lowest-lying atomic excited states of krypton and/or of the correlated molecular states is performed in the neighborhood of the first atomic level (${}^3P_1$). Indeed, relaxed excimer formation takes place only through collisions, since direct formation from the ground state is not possible because of the short-distance ground-state repulsive potential. These kinetic processes have been widely studied (see Refs. [8,9] and references therein) and the knowledge of the kinetic times associated with relaxed excimer formation allows a precise monitoring of the second excitation, which leads to highly excited excimer state formation at a short internuclear distance. The principle of this two-step excitation is sketched in Fig. 1. The $Kr_2$ potential curves are taken from Ref. [6].

The detailed experimental setup will be described elsewhere. Briefly, in the first step vuv selective excitation is obtained by a monochromatized laser plasma source [10]. The second step is performed using a tunable pulsed dye laser pumped by a YAG (YAG denotes yttrium aluminum garnet) laser (10 ns) and a Raman cell allowing one to probe in the range 950–1000 nm. The tunable time delay between the two laser beams is performed with nanosecond accuracy. The experimental device allows one to work at up to 0.2-$\mathrm{cm}^{-1}$ resolution in a pressure range extending from 150 to 2000 hPa.

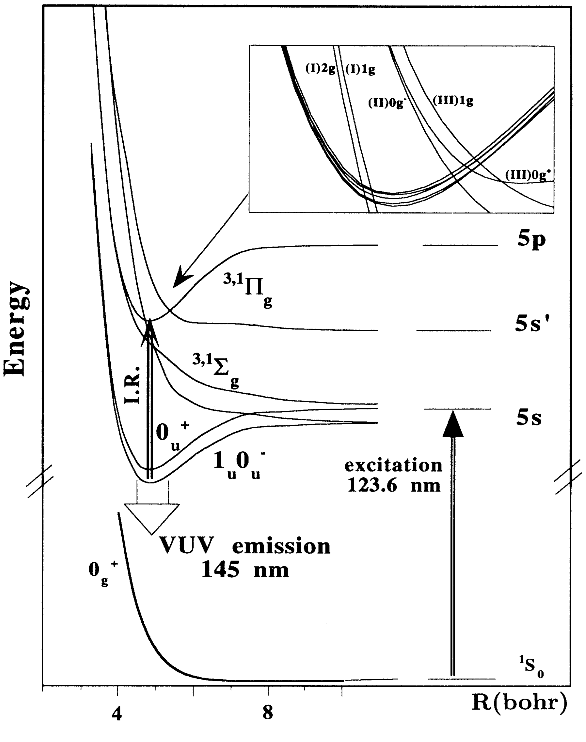

FIG. 1. Schematic description of molecular states involved in the present experiment. The arrows represent the two excitations performed and the emission detected (second continuum). The inset shows the calculated potentials including spin-orbit coupling for ${}^{3,1}\Pi_g$ parent states. The repulsive states are labeled on the figure; the attractive states at increasing energies are $(\mathrm{III})0_g^-$, $(\mathrm{IV})1_g$, $(\mathrm{IV})0_g^+$, (II)2*g*, and $(\mathrm{V})1_g$.

1050-2947/95/51(4)/3351(4)/$06.00

The first result of such an experimental approach is a direct discrimination between atomic and molecular species. Figure 2 shows time-resolved fluorescence profiles. The profiles of Fig. 2-I show the reduced fluorescence in the case of a 400-ns delay between the two excitations. At such times, the vuv fluorescence at 145 nm is mostly that of the relaxed $^3\Sigma_u^+(1_u,0_u^-)$ excimers. The effect of the reduced fluorescence at a molecular absorption wavelength is thus very large and occurs in a few nanoseconds. On the contrary, the profiles of Fig. 2-II show the excimer reduced fluorescence which occurs when atomic reexcitation occurs, i.e., at a short time delay (30 ns) between the two excitations. At such early time delays the products of the first excitation are still mainly nonrelaxed molecular and atomic species [8]. The second excitation reduces the precursors of the observed fluorescence and the LRF effect is thus extended on the whole time scale. By recording the amplitude of the reduced fluorescence and tuning the reexcitation wavelength, the spectra displayed in Fig. 3 are obtained. In Fig. 3-I the spectra obtained after a long time delay are shown. Absorption occurs from the relaxed $^3\Sigma_u^+(1_u,0_u^-)$ state towards higher, excited, molecular *g* states. These molecular bands do not exist in the spectrum displayed in Fig. 3-II. Indeed, the $^3\Sigma_u^+(1_u,0_u^-)$ relaxed state is almost not populated 30 ns after the excitation, as seen from Fig. 2-II, curve A. This spectrum shows only an atomic line arising from the $5s[3/2]_1$ ($^3P_1$) [11] level. It has to be noticed that the atomic line lies in the immediate neighborhood of an observed molecular band. Nevertheless, neither the shape nor the peak position coincides.

The one-photon absorption from the relaxed level of the $^3\Sigma_u^+(1_u0_u^-)$ state allows one to probe *g* states. According to our previous preliminary experimental results [7] in the visible wavelength range and to our *ab initio* calculations [6], the observed molecular profiles can be separated into two groups. The first one can be assigned to $^{3,1}\Sigma_g \leftarrow {}^3\Sigma_u^+$ transitions and the second one to $^{3,1}\Pi_g \leftarrow {}^3\Sigma_u^+$ transitions. In the infrared the first group should correspond to bound-free transitions since $\Sigma_g$ states are purely repulsive in this range. This theoretical result is also supported by the observations of Arai *et al.* [2] who reported a broad absorption near 1300 nm. In the range 955–995 nm, a limited number of bands correspond obviously to bound-bound transitions. The four main bands early observed [1] have never received, until now, a clear fine-structure assignment. The calculated spectrum allows a safe assignment of these observed bands.

As shown in Fig. 1, the *g* states involved in the bands assigned to the observed transitions are electronic states of $^{3,1}\Pi_g$ parentage. These states have the same $[^2\Sigma_u^+]\pi_u np$ character in the whole internuclear distance range of interest and have only one strongly localized crossing. Thus a diabatic representation of these states shows attractive potentials correlated with the 5*p* atomic

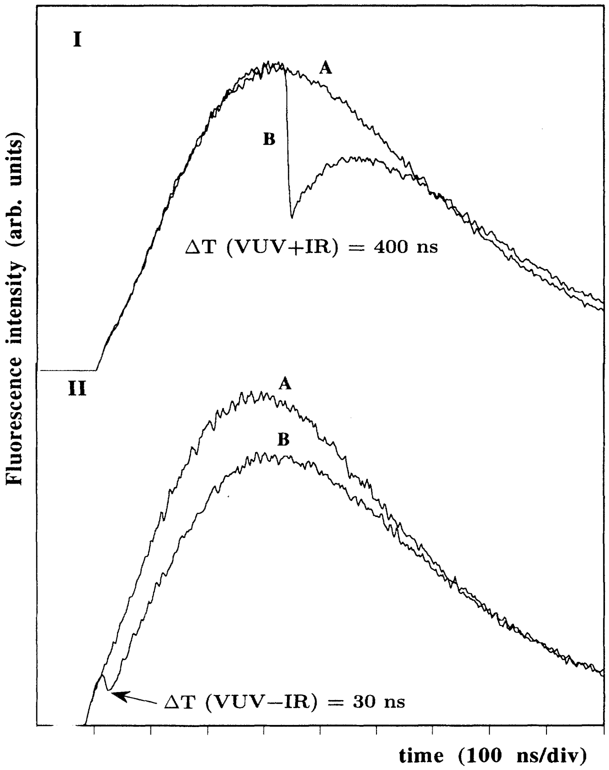

FIG. 2. Illustration of vuv (145-nm) laser reduced fluorescence for two different excitation delays (Δ*T*). The krypton pressure is 400 hPa. Curve A, vuv excitation only; curve B, vuv and ir excitation.

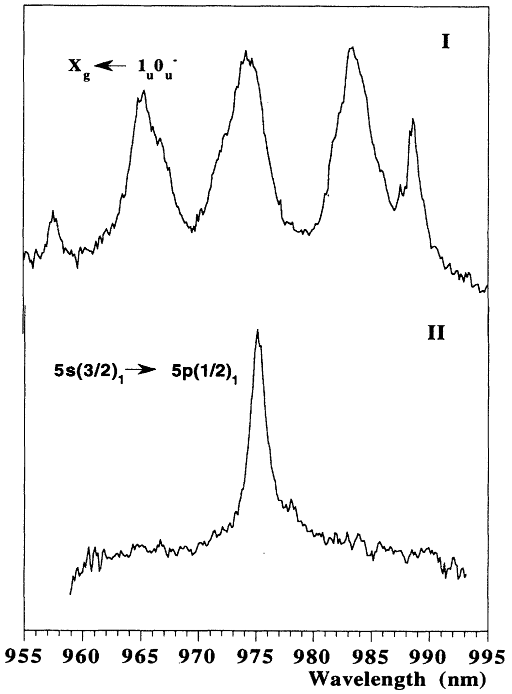

FIG. 3. LRF spectra (krypton pressure of 400 hPa, wavelength in air) I, spectrum obtained with $\Delta T = 400$ ns between the two excitations showing molecular structures; II, spectrum obtained with $\Delta T = 30$ ns between the two excitations exhibiting only an atomic structure.

levels, crossed by repulsive potentials correlated with 5*s* or 5*s*′ atomic levels (Fig. 1). Taking account of spin-orbit coupling, $^{3,1}\Pi_g$ states are split into five states: one $0_g^-$, one $0_g^+$, two 1*g*, and one 2*g*, as shown in the inset of Fig. 1. Yet all these states exhibit a deep potential well with an equilibrium distance close to the one of the $^3\Sigma_u^+(1_u,0_u^-)$ state, i.e., 5.22 bohr (2.761 Å) [6]. The calculation of Franck-Condon factors, including *ab initio* transition moments, leads to the determination of the vibronic transitions and their relative intensity. The transition moments between (1) $1_u$, (I) $0_u^-$, and the five $\Omega$ states related to $^{3,1}\Pi_g$ states were computed using the relativistic wave function obtained with the CIPSO algorithm of Ref. [6]. Using the $\Omega$ potential curves for $1_u,0_u^-$ and the diabatic potential curves for the upper states, the vibrational levels and the relative intensities were determined for the 0-0 vibronic transitions. The calculated spectra are then obtained assuming a Lorentzian profile for each line. As mentioned above, the involved molecular states are predissociative with crossings either in the neighborhood of the $v=0$ level [(IV)$1_g$,(II)2*g*] or near the $v=2$ level [(III)$0_g^-$,(III)$0_g^+$,(V)1*g*]. The linewidth of the observed bands is thus expected to be dominated by predissociation processes. This phenomenon is taken into account by an empirical width for the basic Lorentzians (the full width at half maximum is assumed to be 10 cm$^{-1}$). The obtained calculated spectrum is presented together with the experimental spectrum in Fig. 4.

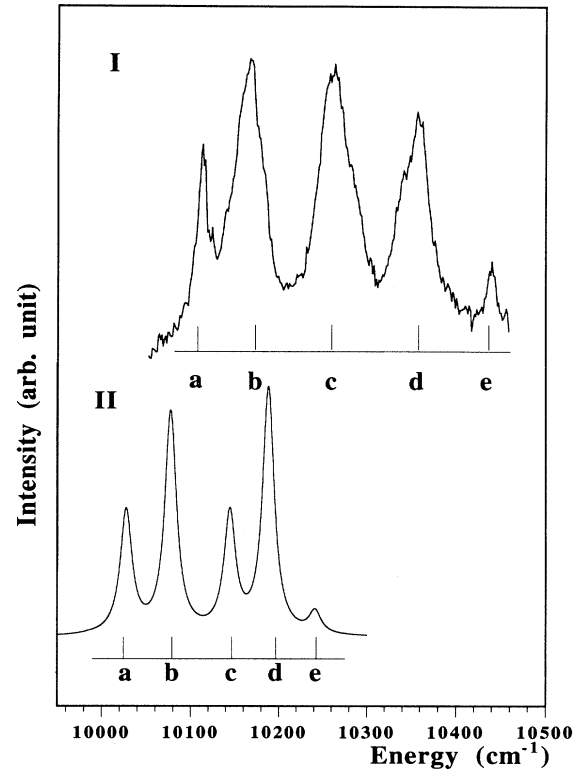

FIG. 4. Comparison of experimental (I) and calculated (II) spectra. The calculated ($v''=0-v'=0$) transitions are as follows: a, (III)$0_g^-\leftarrow$(I)$1_u$; b, (IV)$1_g\leftarrow$(I)$0_u^-$; c, (IV)$0_g^+\leftarrow$(I)$1_u$; d, (II)$2_g\leftarrow$(I)$1_u$; and e, (V)$1_g\leftarrow$(I)$0_u^-$.

It must be stressed that the calculated spectrum is obtained without any energy correction. This result may be considered as a remarkable test of the *ab initio* calculation accuracy. The agreement concerns both the energy splitting and the intensity. We believe that a residual atomic contribution (at $\lambda=975.17$ nm) may contribute to the experimentally observed intensity, increasing the relative intensity agreement between the experimental and calculated spectra. The five observed bands are unambiguously assigned to absorption from the $^3\Sigma_u^+(1_u,0_u^-)$ state towards the five *g* states associated with $^{3,1}\Pi_g$ parent states (Table I). This assignment allows one to check the reality of a fine structure in a krypton excimer. It may be noted that the splitting between the five states cannot be observed for highly excited molecular states. Actually, according to calculations, in the infrared the five states lie in an energy range of 200 cm$^{-1}$. The second group of $\Pi_g$ states lies 20 000 cm$^{-1}$ above (I)$1_u0_u^-$ (transition near 500 nm) and the five corresponding states lie in an energy range of 40 cm$^{-1}$. Our preliminary experimental result in the visible spectrum [7] has confirmed no clear evidence for the splitting of $\Pi_g$ states.

The results of transition moment calculations allow

TABLE I. Wavelength and energy of the five observed transitions together with the given interpretation. The wavelength is given in nanometers in air. The results are compared with previous experimental observations in the same wavelength range.

| Arai *et al.* [2] | Kasama *et al.* [3] | Kane *et al.* [5] | This work (zero density in air) | Transition energy (cm$^{-1}$) | Attribution | Theoretical moments (a.u.) |
|---|---|---|---|---|---|---|
| | | 958 | 957.19 | 10 444 | (V)$1_g\leftarrow$(I)$0_u^-$<br>(e) | 1.14 |
| 965.3 | 965.5 | | 965.19 | 10 358 | (II)$2_g\leftarrow$(I)$1_u$<br>(d) | 3.80 |
| 974.3 | 974.3 | | 973.92 | 10 265 | (IV)$0_g^+\leftarrow$(I)$1_u$<br>(c) | 2.66 |
| 983.3 | 983.3 | | 983.39 | 10 166 | (IV)$1_g\leftarrow$(I)$0_u^-$<br>(b) | 3.63 |
| 988.6 | 988.6 | | 988.56 | 10 113 | (III)$0_g^-\leftarrow$(I)$1_u$<br>(a) | 2.70 |

one also to assign clearly the initial state of the observed transitions. Indeed, for each final state, there is a nonzero transition moment either from the (I)$1_u$ or from the (I)$0_u^-$ state. The corresponding moments are reported in Table I together with the present experimental results and previous observations. It should be noted that our measurements are in good agreement with previous ones at lower resolution. The recent work by Kane *et al.* [5] shows a partly saturated infrared absorption spectrum in this wavelength range. The main lines are thus not investigated in their work, but the transition with the lowest transition moment is observed near 958 nm. Other low-intensity structures have also been evidenced by these authors and should be understood in terms of vibronic structure ($\Delta v = 1$). Such a discussion is beyond the scope of the present work. These vibronic structures, together with the ones observed for higher excited states, are under analysis. As noted above, the broadening of the lines is governed by predissociation processes. Yet for the lower-energy band [transition (I)$1_u \rightarrow$(III)$0_g^-$] preliminary results attempted at higher resolution show structures unobserved on the other bands and also have to be analyzed in terms of rovibronic transitions ($\Delta v = 0$), suggesting a possible non-predissociative character for the first (III)$0_g^-$ state vibrational levels. Such work is still in progress.

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