CROATICA CHEMICA ACTA CCACAA 59 (3) 643—652 (1986)

YU ISSN 0011 1643
CCA-1676 UDC 541
Original Scientific Paper

Optical Transitions in Highly Excited States: RF LOG Spectrum of XeI

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Received September 17, 1985

Pulsed laser optogalvanic spectroscopy of diluted gases in a 32 MHz radio frequency discharge (RF LOG) was applied to xenon in a pressure range from 0.01 to several Torr. The optical transitions caused by exciting the products of the discharge with laser energies from 14,000 to 17,000 cm^{-1} have been recorded and assigned. At low pressures, most transitions originate in the 5d states, whereas at higher pressures those from the 6p and 6s' states become dominant. Results indicate that (jl) coupling and selection rules $\Delta J = 0, \pm 1$ and $\Delta K = 0, \pm 1$ provide the most appropriate description of the observed transitions to the lower n-states. However, some transitions with $\Delta K = \pm 2$ also possess considerable intensity for some higher angular momentum transitions (p—d, d—f). The low pressure spectra are dominated by the d—f transitions for which all series have been observed. An important feature of these series is that at high n values ($n > 20$) the oscillatory potential of the RF field starts to populate high angular momentum states and causes a substantial broadening of the transitions to these states. In addition, close to the ionization limit, field induced ionization can take place and, under certain conditions, this may cause certain high series members to disappear. The corresponding results are presented and discussed.

Atomic spectroscopy[1] has provided the basic information and played the dominant role in the development and growth of quantum theory. The continuous interplay of experiment and theory has characterized this development and, even today, it continues to produce new insights into the behaviour of electrons in atoms and molecules. In particular, the advent of the laser and its use in conjunction with discharges, particle beams and strong electric and magnetic fields has revolutionized the study of high-excited states. A plethora of new techniques have evolved, and certain results derived from them constitute a strong challenge even for atomic theory.

We present here results for some highly-excited states of xenon. These results were obtained by laser optogalvanic (LOG) spectroscopy of 32 MHz radio-frequency (RF) discharge in a diluted gas in a closed system. Pulsed dye-laser excitation in the wavenumber range 14000—17000 cm^{-1} was used. This work is a continuation of previous RF LOG studies of xenon[2]. The LOG

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Supported by the U. S. Department of Energy.

method[3,4], in several modifications, is particularly suitable for the generation and study of highly-excited states of atoms and molecules. In particular, the RF discharge[5] has the distinct advantage that the electrodes, being external, are not subject to attack by the gas under investigation.

Several studies of xenon using RF LOG variants have appeared recently[5-9]; taken in conjunction with recent results on the properties of highly-excited states obtained by other methods[10-12], xenon has become an important test case for the development of theories and models for the interpretation of complex atomic spectra[13-18]. Indeed, spectra are now readily obtained in steady, pulsed or oscillatory electrical and magnetic fields, and the effects of collisions of these highly-excited, Rydberg, states with inert and reactive gases or absorption of blackbody radiation by them are readily measured[19]. And, finally, the ready accessibility of atoms and molecules in exotic states which had previously been known only from astrophysical observations provides a strong impetus for intense study.

EXPERIMENTAL

Several aspects of our technique are original[2]: the use of a pulsed laser, the external supply of RF power and external signal pick-up. Since a pulsed laser was used, the signals had to be normalized before averaging on a pulse-by-pulse basis; and, since the pulse repetition rate was low, the effective duty-cycle had to be forced toward unity in order to obtain smooth high resolution spectra. Closed systems (quartz tubes of Φ 5 mm) and xenon pressures between 0.04 and 1 Torr were found to be optimal for the maintenance of a stable discharge and for the study of pressure effect. The RF field, as supplied by two externaly-mounted copper electrodes, when brought into resonance with the discharge required powers of only a watt or so to sustain stable discharge — an important consideration because both the pressure and the discharge intensity may shift and broaden the spectral lines. Excellent LOG signals were obtained when the pick-up coil was displaced relative to the RF electrodes and when a transverse optical excitation was imposed in the region between the pick-up coil and the RF electrodes. The cell configuration, excitation and pick-up are shown in Figure 1. A Chromatix CMX-4 flash lamp pumped dye laser operating in the region 14000—17000 cm^{-1} was used for excitation.

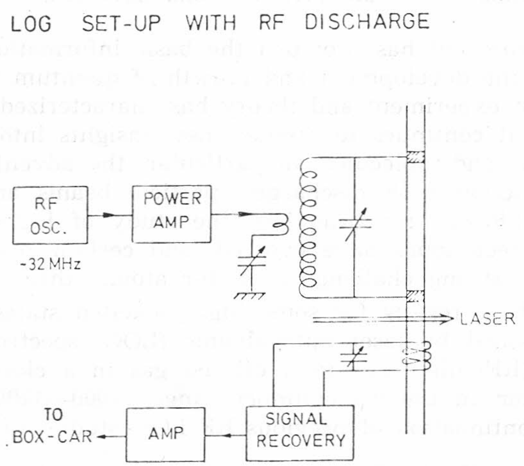

Figure 1. Cell configuration, excitation and pick-up of the optogalvanic signal

RESULTS AND DISCUSSION

The topic of interest is the effect of gas pressure on the RF LOG spectra of xenon. In discussing these effects one must keep in mind the electronic configuration of the xenon atom, as well as the characteristics of the technique that produces the LOG signals in the RF discharge.

In xenon, a rare gas with a closed valence shell configuration... $5s^2\,5p^6\,(^1S_0)$ in the ground state, the excitation of a p electron yields two $5p^5nl$ configurations one with a $^2P_{3/2}$ core (nl-states) and the other with a $^2P_{1/2}$ core (nl'-states). Thus, all levels of XeI in which we are interested may be considered as built on either the $^2P_{1/2}$ or $^2P_{3/2}$ state of the ionic core. The coupling scheme that best describes these levels is (jl)-coupling in which electrostatic interactions are weak compared to the spin orbit interactions of the core (i. e., the parent ion) but strong compared to the spin orbit coupling of the optical (i. e., the external) electron. The total angular momentum j of the parent ion (either 3/2 or 1/2, as stated) and the orbital angular momentum l of the external electron (0, 1, 2, 3, for s, p, d, f, respectively) couple to form a resultant K, which then couples with the electron spin ($\pm 1/2$) to yield J. According to this scheme, level designations are $nl\,(K)\,J$ and $nl'\,(K)\,J$ and the optical selection rules for dipole transitions are $\Delta j = 0$; $\Delta K = 0, \pm 1$, and $\Delta J = 0, \pm 1$, $0 \leftarrow\!|\!\rightarrow 0$.

The experimental term scheme[21] of XeI is shown in Figure 2. Because of the large splitting of the ionic core (~ 10000 cm^{-1}), most nl' levels are autoionizing levels located above the $^2P_{3/2}$ threshold to which the nl series converge. Those wich lie below the $^2P_{3/2}$ threshold may be strongly perturbed by channel interactions: thus, rare gas spectra often exhibit large shifts of energy and intensity because of interaction between levels of the same parity and J (e. g. np by np'). In xenon, however, only 6p$'$, 5d$'$ and none off the nf' levels lie below $^2P_{3/2}$ limit and, therefore, these effects are small. Unfortunately, even the (jl)-coupling model is not entirely satisfactory: nominally forbidden transitions for which $\Delta j \neq 0$ are observed (e. g. s$'$—p, s$'$—f, d—f$'$); the intensities of nominally allowed transitions do not maximize when $\Delta K = \Delta J$; and transitions with $\Delta K = 2$ are frequently observed.

The RF LOG technique depends on the interplay of several events in order to yield a spectrum: the RF discharge creates an pseudo equilibrium set of excited states, which set depends sensitively on frequency, power, local temperature and pressure. In addition, the RF discharge may produce large variable electric and magnetic fields which (vide infra) have severe consequences for the fate of high series members. The discharge itself is probed by a tunable laser beam which, when absorbed, changes the equilibrium set. The shift in this equilibrium and/or the process (rate) of equilibrium restoration produces a change of discharge impedance which is detected by a pick-up coil, thus producing the so-called optogalvanic signal.

The recorded spectrum, then, depends on the density and lifetime of the absorbing states in the discharge, the transition probability to higher excited states and, particularly, on the impedance change that this process produces in the discharge. As a result, the LOG signals may be either positive or negative. Indeed, it is entirely possible that certain transitions will produce no signal at all, in which case the absence of signal does not imply the

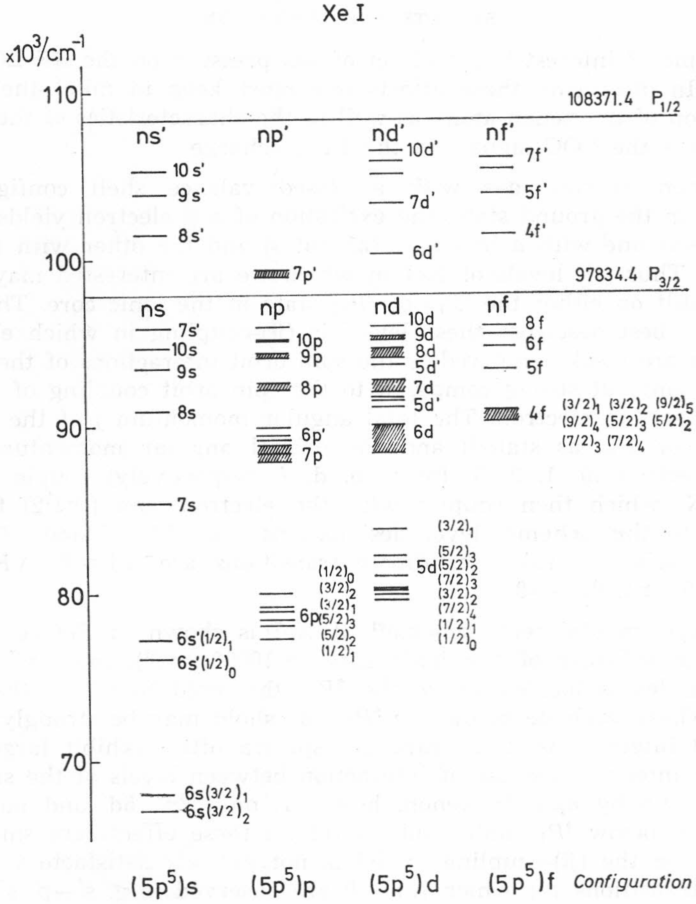

Figure 2. Partial term diagram for xenon[21]

absence of such transitions. Under our conditions, when the laser excitation occurs at the edge of the discharge only positive signals are observed.

The low resolution ($\Delta\nu \sim 3\ cm^{-1}$) RF LOG spectra of 40 and $\sim$950 mTorr xenon in a 32 MHz discharge ($\sim$1 W), obtained as described (see Experimental), are shown in Figures 3, 4, and 5. The regions 14000—15000 cm^{-1}, 15000—16000 cm^{-1} and 16000—17000 cm^{-1} are shown in the upper (a) and lower (b) parts, respectively, of these figures. It is evident that higher pressures produce large alterations of the spectrum. For example, the intensities of the spectral lines change both relatively and absolutely.

As indicated in the figures, the low pressure spectra are dominated by seven composite series of 5d-nf transitions. An eigth series, which originates from the 5d$(3/2)_1$ level, terminates below 14000 cm^{-1} (see Table I) and was not subjected to much study*. Some of the 5d-nf series have been reported

* Footnote: We have been able to detect some members of this series in the region above 13870 cm^{-1} i. e. close to its limit at 13944 cm^{-1}; but, because of the low laser power available to us in this region, no significant study of this series was attempted.

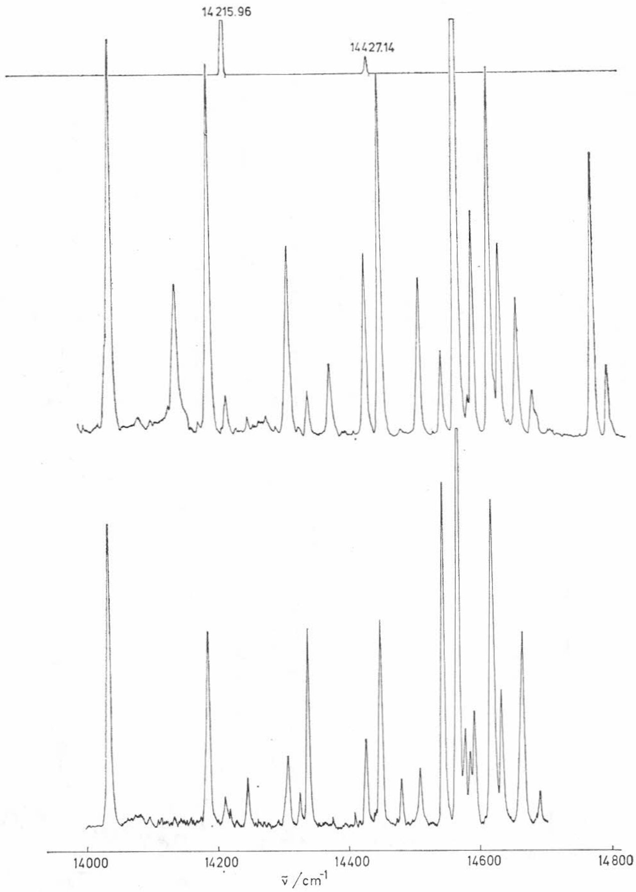

Figure 3. Low resolution RF LOG spectra of 40 mTorr (upper part) and 950 mTorr (lower part) xenon in a 32 MHz discharge recorded from approximately 14000—15000 cm^{-1}.

TABLE I

Observed d—f Transitions Between 14000 and 17000 cm^{-1}
Upper level *nf*

Lower level	$[3/2]_1$	$[3/2]_2$	$[5/2]_2$	$[5/2]_3$	$[7/2]_3$	$[7/2]_4$	$[9/2]_4$	$[9/2]_5$	*n*	limit (cm^{-1})
$5d[1/2]_0$	+								6—10	18062
$5d[1/2]_1$	+	+	+						6—11	17847
$5d[3/2]_1$	ends below 14000 cm^{-1}								limit	13944
$5d[3/2]_2$	+	+	+	+					6—14	17511
$5d[5/2]_2$			+	+	+				8-lim	15908
$5d[5/2]_3$		+	+	+	+	+	+		3-lim	15403
$5d[7/2]_3$				+	+	+	+		7-lim	16863
$5d[7/2]_4$				+	+	+	+	+	6—13	17637

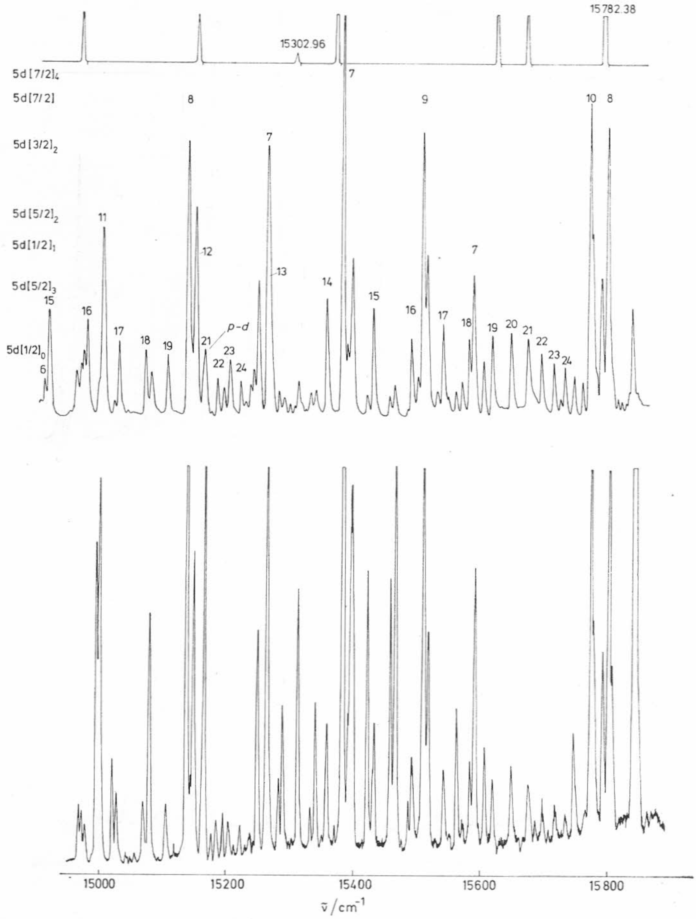

Figure 4. Low resolution RF LOG spectra of 40 mTorr (upper part) and 950 mTorr (lower part) xenon in a 32 MHz discharge recorded from approximately 15000—16000 cm^{-1}.

recently[2,7,9]. The newly reported series presented here are the 5d $(5/2)_2 \rightarrow nf$ and 5d $(5/2)_3 \rightarrow nf$ series, with limits at 15908 and 15403 cm^{-1}, respectively. The former consists of transitions to $(5/2)_2$, $(5/2)_3$, and $(7/2)_3$ and the latter to $(3/2)_2$, $(5/2)_2$, $(5/2)_3$, $(7/2)_3$, $(7/2)_4$, and $(9/2)_4$ nf-levels. This last series as well as the 5d $(1/2)_1 \rightarrow$ nf $(5/2)_2$ (Table I), violates the (jl)-selection rules.

The results of Table I were obtained at high resolution. That is, once the location of a composite series member was determined in the low resolution spectrum, its components, their intensities, and exact positions were measured using an intracavity etalon of about 5 cm^{-1} free spectral range. These scans were always initiated at a calibration marker (neon hollow cathode lamp), further calibration being performed by means of fringe counting to an accuracy of about 0.2 cm^{-1}. As an example, the highly resolved part of the RF LOG spectrum at 16730 cm^{-1}, shown in Figure 6., exhibits several d-f series members (i. e., 10f from 5d $(1/2)_1$, 11f from 5d $(7/2)_4$, 12f from 5d $(3/2)_2$ and 28f-31f from 5d $(7/2)_3$) and one p-d transition (i. e., 6p $(3/2)_2 \rightarrow$ 10d $(5/2)_3$.

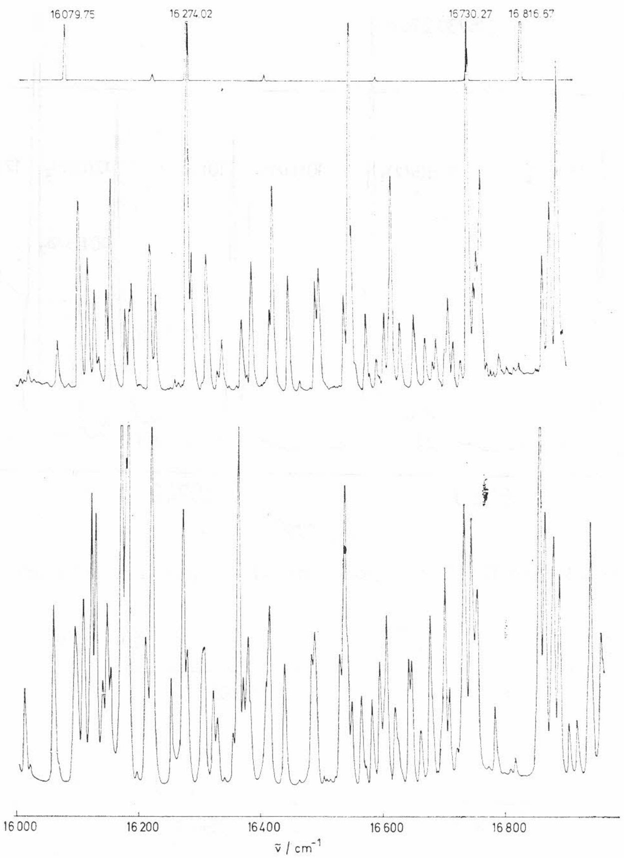

Figure 5. Low resolution RF LOG spectra of 40 mTorr (upper part) and 950 mTorr (lower part) xenon in a 32 MHz discharge recorded from approximately 16000—17000 cm^{-1}.

Once accurate energies of the observed lines are known, the energies of the higher nf-levels can be readily determined. In Figure 7. these values are shown diagramatically for $n = 8$ to 12 indicating that with increasing n the energy separations of the levels decrease rapidly. Indeed, at $n = 20$, this K-span extrapolates to less than 2 cm^{-1}, a fact that is of some help in explaining the behaviour of the high series members which, as stated,[6,8,9,13] collapse and disappear before reaching the ionization limit. This gradual collapsing is evident in Figure 6. for the $n = 29$f—31f members of the 5d $(7/2)_3$-nf series.

At which member the nf series disappears depends primarily on discharge conditions: the weaker the discharge the greater is the chance to observe those series members that lie close to the ionization limit. Since the disappearance of the bands is undoubtedly connected to an ionization process, it is reasonable to assume that field ionization is the culprit. That is, in the high energy states for which $n > 30$, the energy provided by the RF filed is adequate to produce field ionization. The other phenomenon, to which we have made reference as

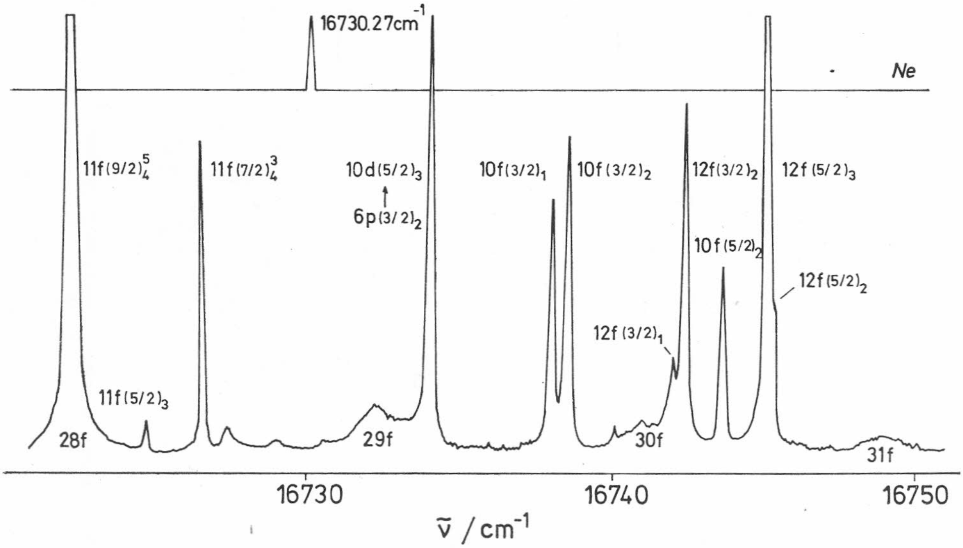

Figure 6. High resolution RF LOG spectrum od 40 mTorr xenon around 16730 cm^{-1}.

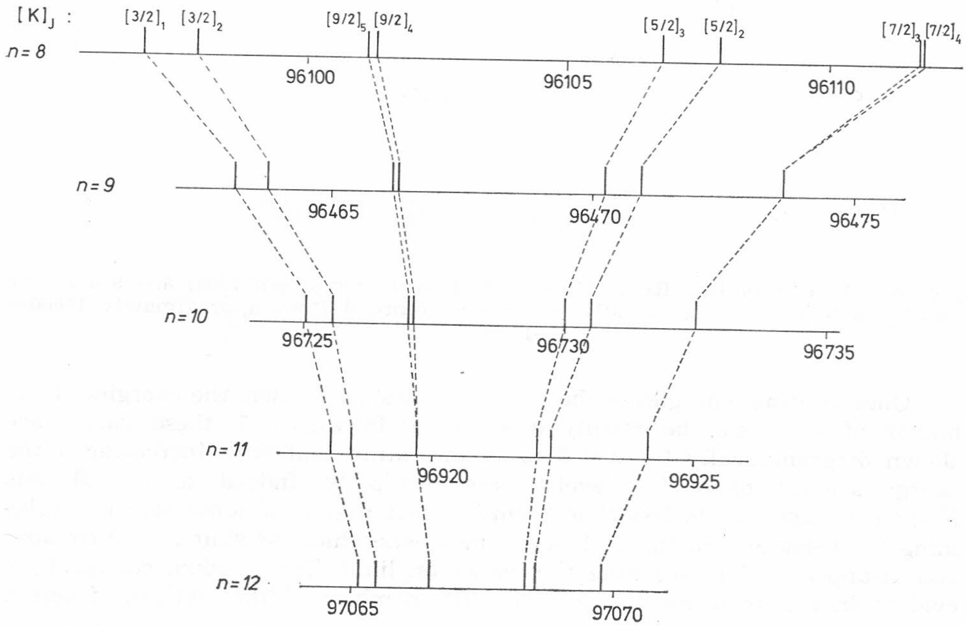

Figure 7. Experimental state energies of xenon nf-states, $n = 8 — 12$

a »collapse« but which really is a massive broadening of the high-n members is also intriguing. This behaviour had been attributed to collisional effects. However, it is now becoming clear that this broadening is attributable to an l-mixing that takes place in the upper state and that it is caused by the presence of electric and magnetic field in the RF discharge. Since the polarizability

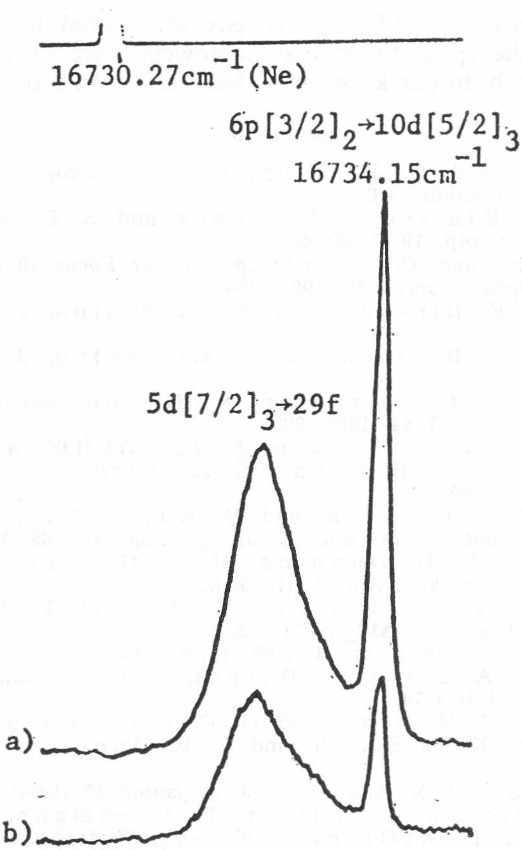

Figure 8. Two recording of the 5d $(1/2)_3 \rightarrow 29$f peak under stronger (a) and weaker (b) RF discharge conditions. (Compare also with Figure 6).

of Rydberg atoms[22] increases as n^6, it is clear that, for high n, relatively weak fields can produce considerable mixing. Two recordings of the 5d $(1/2)_3 \rightarrow 29$f peak are shown in Figure 8. under stronger (a) and weaker (b) discharge conditions. It has been shown[7,9] that such xenon peaks split into complicated but interpretable patterns in a magnetic field of about 1—2 T; however, in that case it was necessary to use an isotopically-enriched sample and a line originating from the 5d $(1/2)_0$ which terminates only in nf $(3/2)_1$ (of Table I) in order to resolve the pattern.

In conclusion, a few words on the pressure effect: the evident effect of increased pressure is that transitions from lower energy and lower angular momentum (s, p) levels become more important. This finding can be explained in two ways: either the existing low power of the discharge is inadequate to provide the requisite energy to the increased number of atoms that would permit attainment of higher energy levels and/or the population of higher energy states is decreased by the greater probability of collisions. Also, our results seem to confirm previous findings that transitions into high p states are of lower intensity — a fact previously atttributed to the interaction of these states with the 7p′ state (Figure 2). However, we have observed several d-p transitions which, to our knowledge, have not been reported before.

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SAŽETAK

Optički prijelazi u visoko pobuđenim stanjima: RF LOG spektar XeI

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Proučavan je ksenon kod tlaka od 0.01 do nekoliko Torra RF LOG spektroskopijom. Asignirani su optički prijelazi izazvani pobuđenjem produkata pražnjenja laserskim energijama od 14000 do 17000 cm^{-1}. Kod niskih pritisaka većina prijelaza potječe od stanja 5d, dok kod viših pritisaka dominiraju prijelazi iz stanja 6p i 6s'. U spektrima kod nižih pritisaka dominiraju prijelazi d-f.