ISSN 1330–0008
CODEN FIZAE4

KCd SPECTRAL FEATURES IN K+Na+Cd+Ar HIGH PRESSURE LAMP

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Received 15 October 1993

Revised manuscript received 12 November 1993

UDC 539.196

Original scientific paper

We present the results of spectroscopic studies of the high pressure K-Na-Cd-Ar discharge lamp. They were compared with the results of K-Hg-Ar discharge lamp. The interesting part of the spectrum was the region around the second resonance potassium line (5p-4s transition) at 404.4 nm and 404.7 nm. There we observed a group of satellite bands which we attribute to the KCd excimer transitions. In the red part of the spectrum a broad KCd diffuse band was observed with peaks at 630 nm and 640 nm. From the comparison with the KHg system, we ascribe these bands to the $2\ ^2\Pi - X\ ^2\Sigma^+$ electronic transitions.

1. Introduction

We have investigated the emission spectrum of a 400 W high pressure lamp filled with K, Na, Cd and Ar using time-resolved technique. KCd molecule is of excimer type (bound excited states and almost entirely repulsive ground state with a very shallow potential well). KCd molecule is interesting as a possible candidate for the tunable laser action in the visible or near IR spectral region [1].

In the present experiment we were interested in spectroscopic studies of excimer satellite bands and excimer diffuse bands in the violet and red region of the discharge spectrum. Using pseudopotential calculations [2] and relevant transition dipole moments we calculated the red diffuse band of KHg excimer. We discuss the similarity between analogous KHg and KCd excimer bands observed in the present experiment and in the experiment with K-Hg-Ar discharge lamp [3].

2. *Experiment*

The experimental apparatus is shown in Fig. 1. The arrangement has been used earlier [3,4]. A high pressure K-Na-Cd-Ar discharge lamp driven with the AC electric current has been used in this experiment. The burner of this lamp was made of a standard alumina tube. The lamp was operated at 50 Hz and 220 V, with the standard inductive ballast resistor and ignition device. The light from the lamp was spectrally resolved by a high resolution Jobin-Yvon monochromator and detected by a photomultiplier. Detected signal was fed into a box-car averager with a gate aperture of 500 μs and a variable aperture delay. The box-car averager was used to sample out the spectrum at the current reversal and at the current maximum. Signal from a photodiode, which monitored the total lamp intensity, was used as trigger signal for the box-car averager. The processed data were recorded on the strip-chart recorder. Unfortunately, we were unable to perform the usual plasma diagnostics (e.g. Abel inversion, etc.), because the translucent alumina burner transmits the diffused (scattered) light from the discharge [5].

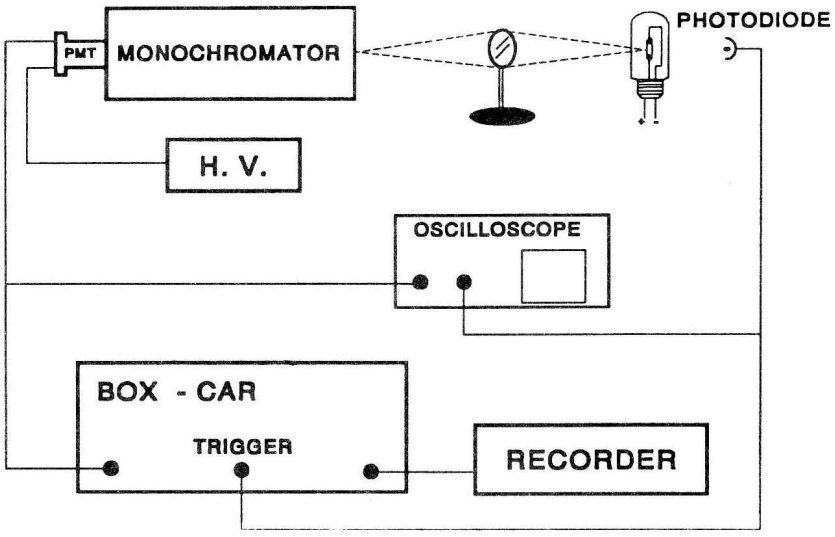

Fig. 1. The experimental set-up.

The relative intensity of the spectral lines and continuum emission of KCd plasmas change drastically from the case of current maximum to current minimum. At current maximum the plasma temperature and electron (ion) density attains its largest values. At this instant many allowed and forbidden atomic spectral lines are visible and they can be easily identified and analyzed. The emission spectra measured at the current reversal instant reflect the conditions of the plasma with lower electron temperature and lower electron (ion) density. In this case the intensities of the atomic lines are much smaller than at current maximum, thus enabling easier observation of all continuous spectral features, i.e. satellites and diffuse bands of molecular origin.

3. Results and discussion

3.1. Satellite bands

In Fig. 2a we present the spectral region of the second resonance line doublet of the potassium (5p-4s) at 404.4 nm and 404.7 nm recorded at current reversal. In the blue and the red wings of that line doublet satellite bands are observed, induced by interaction of the excited potassium atoms with potassium [6] (S_2 and S_3) and cadmium (S_1, S_4, S_5, S_6 and S_7) atoms in the ground state (see Table 1).

When we compare these results (Fig. 2a) with the analogous part of K-Hg-Ar (Fig. 2b) high pressure lamp spectrum [3] we can observe interesting similarities. They indicate a close relation between the relevant KCd and KHg potential energy curves. Fig. 3 presents potential energy curves for the KHg system [2] which tend asymptotically to the different energy levels of mercury and potassium atoms. Due

*TABLE 1. The peaks of three red satellite bands and five blue satellite bands in the emission spectrum of K-Na-Cd discharge lamp are denoted by λ (*nm*) and E (*cm^{-1}*). Their corresponding energy separations from the 404.7* nm *potassium line are denoted as ΔE (*cm^{-1}*).*

S_i	E (cm^{-1})	λ (nm)	interaction	ΔE (cm^{-1})
blue wing				
S_1	24 999	400.0	K-Cd	290
S_2	24 854	402.5	K-K	136
red wing				
S_3	24 552	407.3	K-K	157
S_4	24 456	408.9	K-Cd	253
S_5	24 260	412.2	K-Cd	449
S_6	23 981	417.0	K-Cd	728
S_7	23 878	418.8	K-Cd	831

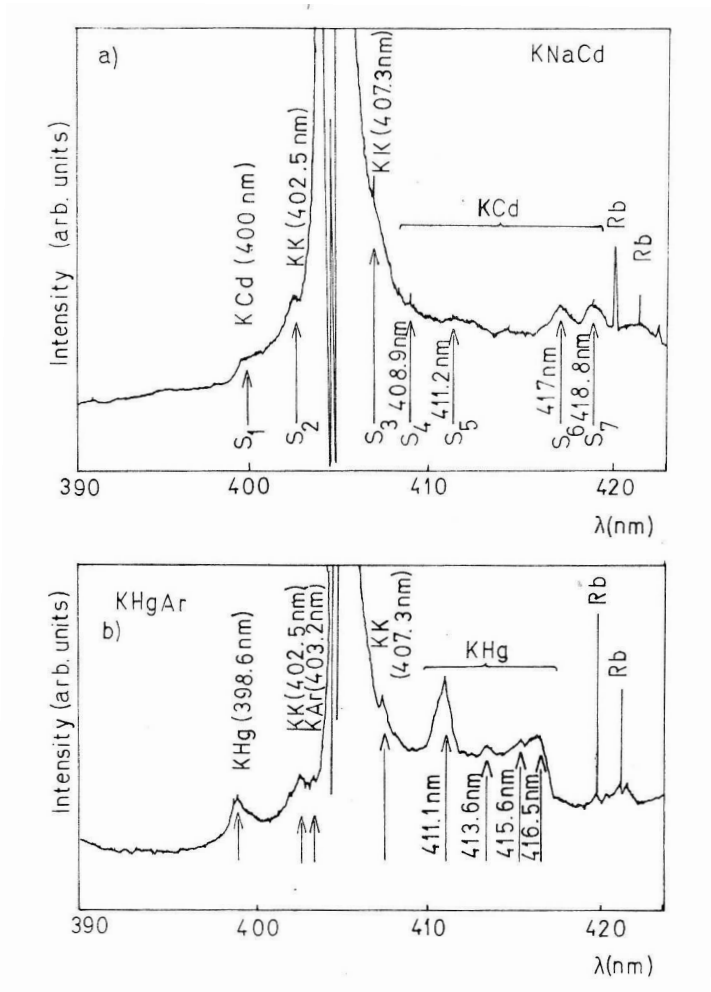

Fig. 2. The spectral region around the second resonance line doublet of potassium (5p-4s) recorder at current reversal for: a) K-Cd-Na *discharge lamp and b)* K-Hg-Ar *discharge lamp.*

to the similarity of these data, we can expect similarity of the origin of the KCd and KHg satellite bands, which could be explained qualitatively by the shape of the corresponding difference potential curves. They should possess extrema corresponding to the satellite band peaks observed in the red and blue wing of the second potassium doublet.

By using potential energies of KHg molecules [2] it is possible to interpret many features which are observed in the visible part of spectrum of KHg high pressure lamp. First, we have paid our attention to the satellite structure in the vicinity of the KHg second resonance doublet ($\lambda = 404.7\,\mathrm{nm}$). This region is defined by radia-

tive transitions from excited electronic states 3 $^2\Pi$ and 5 $^2\Sigma^+$ (asymptotic level K 6 ^{2}P + Hg ^{1}S) to the ground molecular state X $^2\Sigma^+$ (asymptotic level K 5 ^{2}S + Hg ^{1}S). In Fig. 4 we present the 3 $^2\Pi$ – X $^2\Sigma^+$ and 5 $^2\Sigma^+$ – X $^2\Sigma^+$ difference potential curves for the above mentioned transitions. Unfortunately, calculated energies for the large interatomic distances, reported in Ref. 2, are shown in the tabulated lists with insufficient numbers of points, so that cubic spline interpolations of the curves can give only qualitative explanation of the spectral features in the vicinity of the second resonanat potassium doublet. The difference potential curve, 5 $^2\Sigma^+$ – X $^2\Sigma^+$ has a pronounced maximum at an interatomic distance $R = 13.04$ a.u. That maximum gives quasistatic singularity at $\lambda = 397.3$ nm what could explain satellite structure at 398.6 nm in the blue wing of the second resonance doublet of the KHg excimer. The difference potential curve 3 $^2\Pi$ – X $^2\Sigma^+$ has an inflection (i.e. $\dfrac{\mathrm{d}}{\mathrm{d}R}[\Delta V(R)] = 0$) at $R = 15.18$ a.u. This inflection we must take with caution, because in this region calculated energies are defined with insufficient numbers of

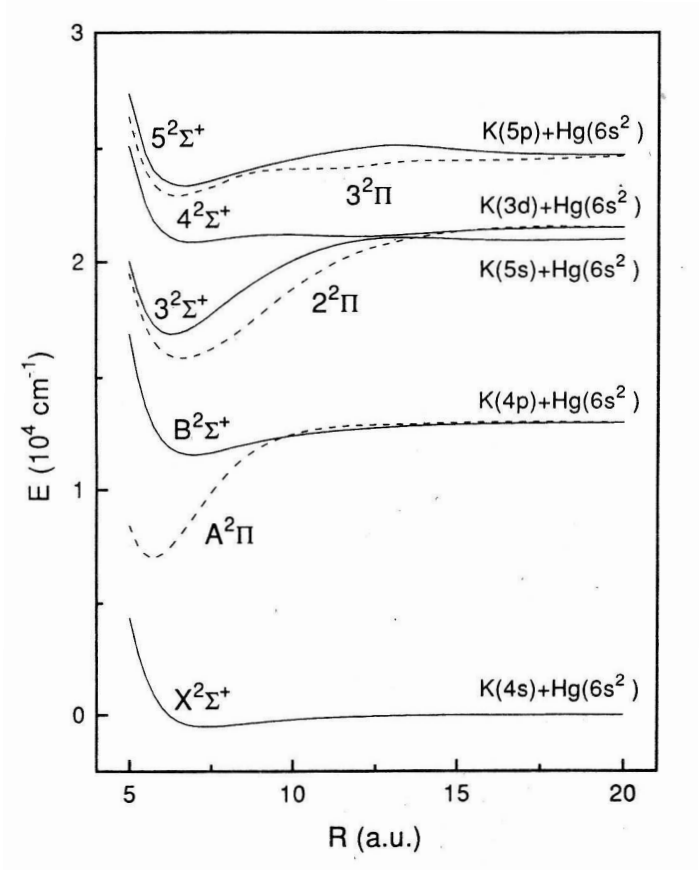

Fig. 3. Potential energies for KHg *system [2].*

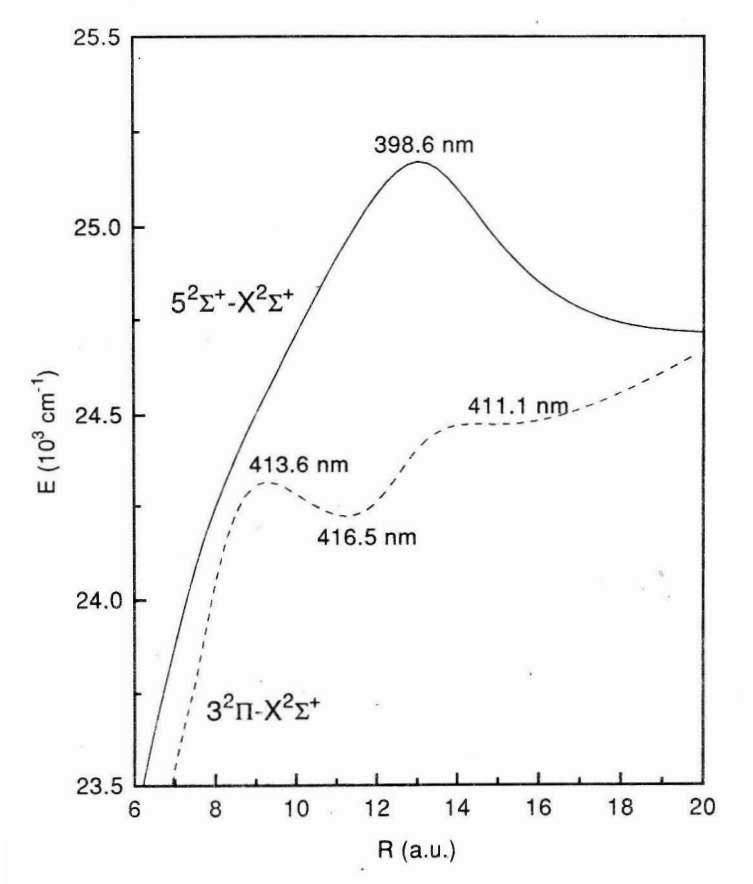

Fig. 4. Difference potential curves $\Delta V(R)$ for optical transitions $3\ ^2\Pi - X\ ^2\Sigma^+$ and $5\ ^2\Sigma^+ - X\ ^2\Sigma^+$ calculated from potential energies.

points. Such curve shape should cause a *cusp* satellite structure [7], with maximum at 408.6 nm. This maximum could be correlated with the *cusp* structure at 411.1 nm observed in the KHg spectrum (Fig. 2b). The maximum and the minimum of $\Delta V(R)$ at $R = 9.3$ a.u., and $R = 11.3$ a.u., respectively, give quasistatic singularities at $\lambda = 411.4$ nm and $\lambda = 412.8$ nm. With so close extrema we could explain the satellite structure at $\lambda = 413.6$ nm and at $\lambda = 416.5$ nm in the KHg case (Fig. 2b). Between these two satellite bands in the spectrum we can see another maximum at $\lambda = 415.6$ nm. We could explain it with interference of three Condon points in the region between the two extrema of the difference potential curve. KHg and KCd are similar molecular systems, because Hg and Cd are neighbouring elements of the same II B group in the periodic system. Because of that, we can make a qualitative comparison of the KHg and KCd spectra.

We have supposed that satellite band peaks at $\lambda = 400$ nm in the blue wing of the KCd second resonance doublet correspond to the extreme of difference potential

curve of 5 $^2\Sigma^+ - X\ ^2\Sigma^+$ transition (Fig. 4). Satellite band peaks at $\lambda = 417$ nm and $\lambda = 418.8$ nm are probably stemming from the neighbouring extrema of $\Delta V(R)$ for 3 $^2\Pi - X\ ^2\Sigma^+$ transition. The satellite band S_5 ($\lambda = 411.2$ nm) is probably stemming from inflection of $\Delta V(R)$ for 3 $^2\Pi - X\ ^2\Sigma^+$ transition. This satellite has not such a *cusp* structure as in the KHg system, probably due to the fact that we have supposed that first derivation of $\Delta V(R)$ at inflection has not a so small value as in the KHg system.

3.2. Red diffuse band

In the part of the spectrum from 550 nm to 700 nm (Fig. 5a) dominates Na resonant D line (3p-3s) at 589.6 nm with Na-Na band at 551.5 nm [8,9] and K-K diffuse band at 572.5 nm [10,11,12]. In the red wing of the sodium D line spreads a diffuse band with two peaks at 630 nm and 640 nm which we attribute to KCd excimer. Analogous band (Fig. 5b) is observed in the emission spectrum of K-Hg-Ar high pressure lamp [3,4] as a result of KHg interaction. Similar bands are observed in the NaHg [13,14,15] and in the NaCd [16,17] system, too. There is no theoretical difference potential curve having an extremum in the corresponding range, so it cannot be a broad satellite rainbow. Czuchaj et al. [2] suggest that this diffuse band stems from transitions from low vibrational levels of C $^2\Pi$ state to $X\ ^2\Sigma^+$ (ground level).

Emission intensity for given transition we can approximate with quasistatic relation:

$$I(\omega) = \frac{8\pi\omega^3}{3c^3} N_A N_B \sum_{g,f} \frac{W_f}{W_g} \frac{4\pi R_c^2 D^2(R_c)}{\left|\frac{dV_{dif}}{dR}\right|_{R=R_c}} e^{-\frac{V(R)}{kT}} . \qquad (1)$$

N_A and N_B are concentrations of A and B atoms; W_f and W_g are statistical weights of final and ground state, R_c is Condon's point at given frequency, $D(R_c)$ is electric dipole moment of corresponding transition, V_{dif} is potential difference and the function $V(R)$ is given by the following relation:

$$V(R) = V_f(R) - V_f(\infty)$$

where $V_f(R)$ is the potential energy of excited molecular electronic state. The theoretically calculated emission spectrum (Eq. (1)) of transition C $^2\Pi - X\ ^2\Sigma^+$ is shown in the Fig. 6 for effective lamp temperature of 1 500 K. This curve with it's shape and maximum of intensity at $\lambda \approx 618$ nm is in good agreement with the present experiment. This transition is typical bound-free excimer transition, with inital state C $^2\Pi$ like bound state, whereas the final state is free ground state. The difference potential curve of these two states is monotonously attractive, so that the maximum of intensity in the spectrum of the observed transition is defined

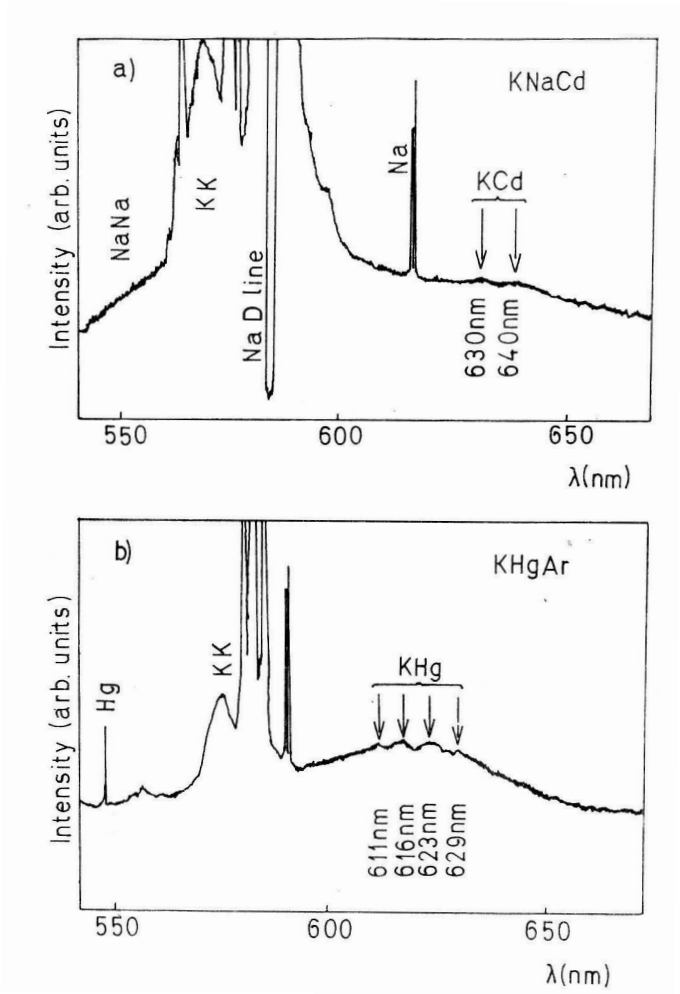

Fig. 5. a) *Part of* K-Cd-Na *discharge lamp spectrum from 550* nm *to 700* nm. *In the red wing of the D line spreads a diffuse band with peaks at 630* nm *and 640* nm. *b) The same part of spectrum of* K-Hg-Ar *discharge lamp with analogous diffuse band (peaks at 611* nm, *616* nm, *623* nm *and 629* nm*).*

by the Boltzmann factor in the relation (1). This factor is the most dominant for transition frequencies from low lying bound vibrational-rotational levels of C $^2\Pi$ bound state to free $X\ ^2\Sigma^+$ state.

In the KHg emission spectrum for oscillations observed at 611 nm, 616 nm, 623 nm and 629 nm (Fig. 5b) we have assumed that they reflect vibrational structure of low lying bound levels in C $^2\Pi$ state. Such oscillations are almost completely washed out in the case of K-Cd-Na-Ar discharge lamp (Fig. 5a).

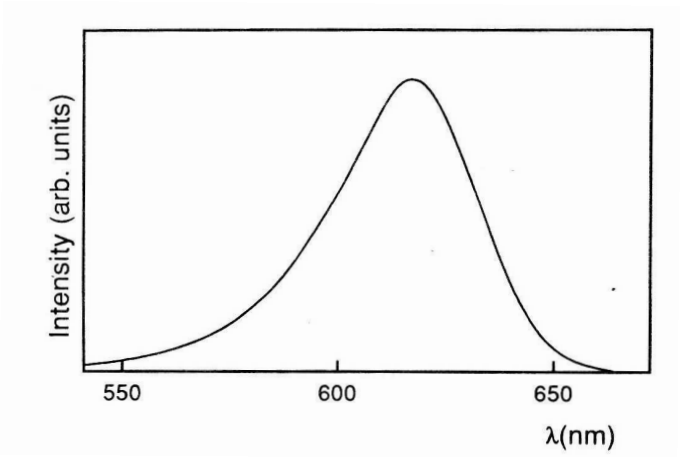

Fig. 6. Theoretically calculated KHg *emission spectrum of transition 3(C)* $^2\Pi - X\ ^2\Sigma^+$ *at* $T = 1\,500$ K.

4. Conclusion

We have presented the results of observation of a emission spectrum of the K-Na-Cd-Ar high pressure lamp. They were compared with results of K-Hg-Ar discharge lamp with the main goal of explaining qualitatively the origin of the diffuse band in the red part of spectrum and satellite structure around the second resonance potassium line.

Acknowledgements

We gratefully acknowledge the financial support from Ministry of Science of the Republic of Croatia, partial support from NIST, USA, project PN-929, Alexander von Humboldt Stiftung (Germany) and Commission of the European Communities (Project under contract N° Cl* / 0525-C (MB)).

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KCd VRPCE U VISOKOTLAČNOJ K+Na+Cd+Ar ŽARULJI

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UDK 539.196

Originalni znanstveni rad

U ovom radu predstavljeni su rezultati spektroskopskih mjerenja visokotlačne K-Na-Cd-Ar žarulje. Ti rezultati su uspoređeni s relevantnim mjerenjima na visokotlačnoj K-Hg-Ar žarulji. U plavom i crvenom krilu drugoga rezonantnog kalijevog dubleta (404.4 nm i 404.7 nm) uočene su satelitske vrpce koje smo pridružili KCd eksimeru. U crvenom dijelu spektra pojavljuje se široka KCd difuzna vrpca s dva vrha na 630 nm i 640 nm. Iz usporedbe s KHg sistemom, ove se vrpce pripisuju $2\ ^2\Pi - X\ ^2\Sigma^+$ elektronskim prijelazima.