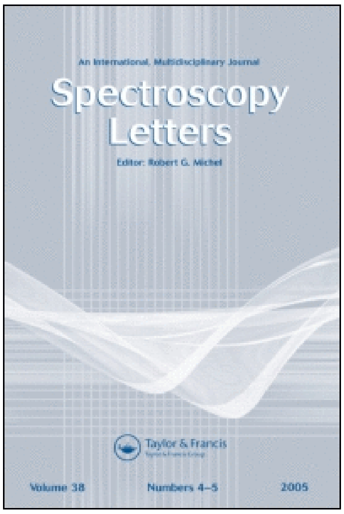

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Electron Energy Loss Under Scattering by Naphthalimide Derivatives Vapours

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To cite this Article Gruzinskii, V. V. , Kukhto, A. V. , Suchkov, V. A. and Kazakov, S. M.(1994) 'Electron Energy Loss Under Scattering by Naphthalimide Derivatives Vapours', Spectroscopy Letters, 27: 1, 65 — 75
To link to this Article: DOI: 10.1080/00387019408002508
URL: http://dx.doi.org/10.1080/00387019408002508

SPECTROSCOPY LETTERS, 27(1), 65-75 (1994)

ELECTRON ENERGY LOSS UNDER SCATTERING BY NAPHTHALIMIDE DERIVATIVES VAPOURS

KEY WORDS: electron energy loss spectroscopy, naphthalimide derivatives, triplet state

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ABSTRACT

Electron energy loss spectra under scattering of electrons on 4-amino-N-(n-butylphenylene)-1,8-naphthalimide and 4-methylamino-N-(o-tolyl)-1,8-naphthalimide in a vapour phase is studied. The primary electron energy was varied from 6 to 60 eV and the scattering angle was 90°. It is found that the differential cross section of excitation of complex organic molecules into some triplet states can reach the same value as singlet ones.

INTRODUCTION

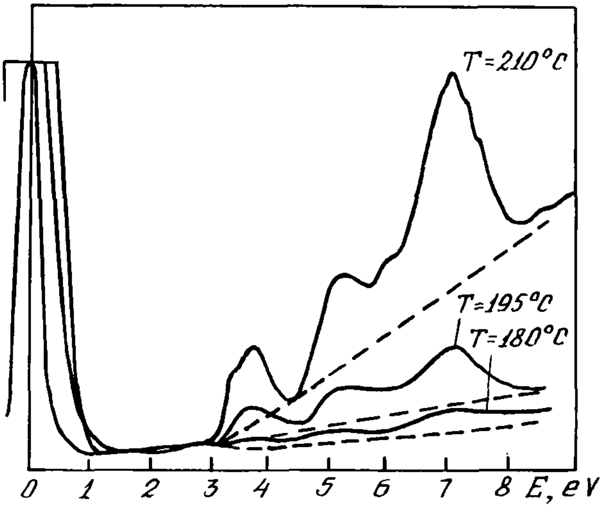
At present a method of electron energy loss spectroscopy is a good alternative to a usual method of photoabsorption spectroscopy and it is wide used to study excitation processes of atomic and molecular shells. The analysis of electron energy loss spectra of complex organic compound vapours can give the information about position and structure of energy levels in a wide spectral region (including levels above ionization potential) and the value of their excitation probability.

In the previous papers[1,2] we studied the structure of electron energy loss spectra under scattering by anthracene, 1,4-bis/2-(5-phenyloxazolyl)/benzene and perylene at low vapour pressures and various energies of exciting electrons in the region E_0=4...600 eV. These complex organic molecules can intensively luminesce and they are the active media of lasers (except anthracene). The electron energy loss spectra and the excitation functions of such big molecules have not been studied before. At low energies near 2...3 eV the bands due to direct excitation of molecular ground singlet state into triplet state T_1 were found. On the basis of these results and the analysis of the changes in electron energy loss spectra at different E_0 it was concluded that for investigated molecules the probability of excitation into triplet states is much lower than into singlet and superexcited ones.

The purpose of this work is to find a new spectroscopic information about molecules 4-amino-N-(n-butylphenylene)-1,8-naphthalimide (compound 1) and 4-(methylamino)-N-(o-tolyl)-1,8-naphthalimide (compound 2) in the gas phase at collisions with low energy electrons. The naphthalimide derivatives are a new class of luminescing and generating organic compounds applicated widely in sciences, medicine and technologies. Some bands in their electronic spectra are due to a charge transfer from one molecular part into another that is their characteristic feature.

EXPERIMENTAL

The detail description of the experimental set-up using in this work can be find in our previous papers[1]. In using electron spectrometer a monokinetic electron beam with a primary energy E_0 passed through a vapour layer. In inelastic collisions the electrons lost a part of their energy which corresponded to excitation energy of various electronic states of molecules. The registration of scattered electrons was carried out at the angle of 90°. An energy resolution was about 0.3 eV. In the papers[1,2] the vapour pressure in the collision cell was about 10^{-3} torr and set on the basis of cer-



Energy loss, eV

FIG.1. Electron energy loss spectra for compound 1 measured at different temperatures. The dashed lines are the device noise.

tain dependences of pressure on temperature. For the naphthalimide derivatives such data are unknown for the present. So in this experiments the reservoir containing investigated substance and the collisional cell were gradually heated to such temperature when electron energy loss spectrum was registered on a required scale. Fig. 1 illustrates such procedure for compound 1. In this figure it is shown a characteristic device noise which is due to scattering of electrons on various elements of electron optics. The noise in-

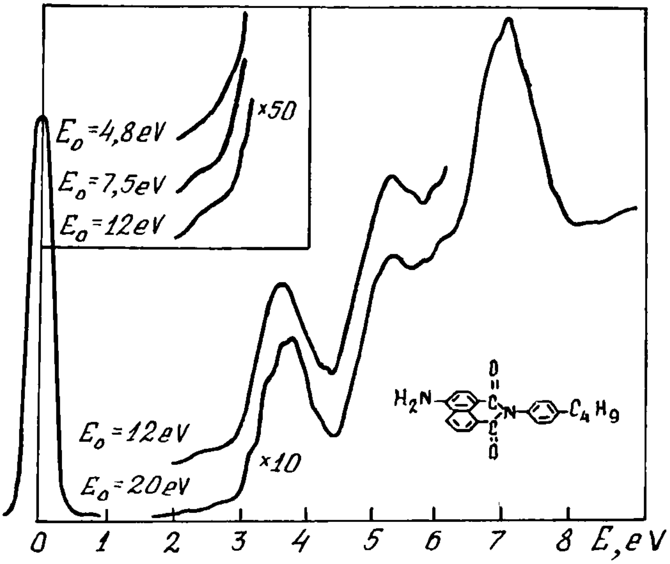


FIG.2. Electron energy loss spectra for compound 1 measured at different E_0.

tensity is risen with molecule concentration in collisional cell. This noise has been subtracted when comparing band intensities in the electron energy loss spectra.

RESULTS AND DISCUSSION

The obtained results are shown in fig. 2 and 3. As in the previous papers[1,2] the most intensive was the band of elastic scattering due to many atoms in these molecules.

It was expected that in a low-energy region 2...3 eV the losses caused by the excitation of molecules

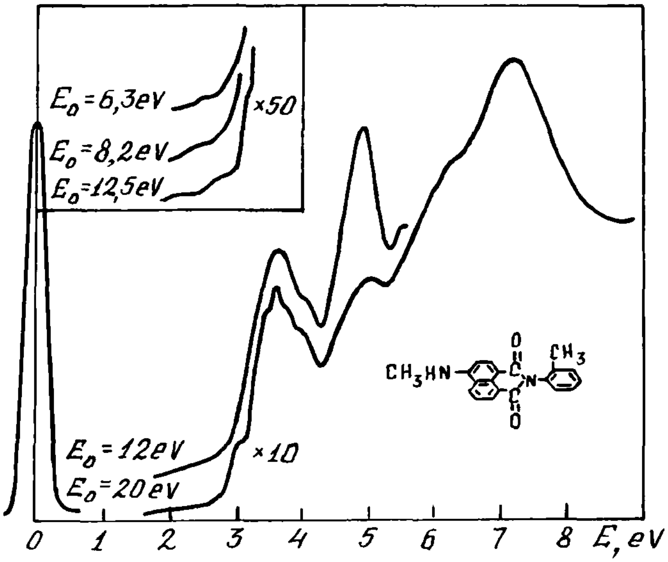


FIG.3. Electron energy loss spectra for compound 2 measured at different E_0.

into lower triplet state will be observed. Fig. 2 and 3 show that at E_0=20 eV in this region there is a low-intensive structure coinciding with a position of lower triplet state. But at lower primary energies this structure (see the fragments of these spectra at upper left corner) does not change essentially in intensity. these data suggest that the effectiveness of excitation of these compounds to the lowest triplet state is small. Thus, the nature of the low-intensive structure observed at E_0=20 eV is not completely clear.

The position of all bands in energy loss spectra and maxima of the optical singlet and triplet transitions taking from optical absorption spectra[5] and triplet-triplet absorption experiments[6] is given in the table. The optical spectra measured in condensed solutions to put in accordance with the energy loss spectra measured in the gas phase is shifted on 0.3 eV as for aminonaphthalimide[7], because for naphthalimides such data are unknown. On the other hand the maxima position in the energy loss spectra is slightly higher due to the existence of a noise.

From the table we can see that the intensive bands with the excitation potentials E=3.39 and 6.9 eV for compound 2 and E=3.62 and 6.97 eV for compound 1 and visible shoulders 6.1(2), 6.16 eV (1) can be identified as due to the singlet-singlet transitions. The intensity ratio of these bands in the energy loss spectra changed little with the energy E_0.

Of greatest interest in obtained results is the behaviour of bands intensities with potentials 5.15 eV for compound 1 and 4.92 eV for compound 2 at different primary electron energies. In this region there is a singlet state S_2 according to photoabsorption spectra (see table). Moreover, the difference between the first and the second intensive bands for both compounds is practically coincided. But when de-

TABLE

Values of bands maxima for compounds 1 and 2 under electron EE and optical OE excitation

Compound	EE bands, eV	OE bands, eV	Transition
1	2.5	2.09	$S_0 - T_1$
	3.62	3.14	$S_0 - S_1$
		4.34	$S_0 - T_2$
	5.15	4.86	$S_0 - S_2$
	6.16	5.94	$S_0 - S_3$
	6.97		$S_0 - S_4$
2	2.5	2.12	$S_0 - T_1$
	3.39	3.12	$S_0 - S_1$
		4.06	$S_0 - T_2$
	4.92	4.87	$S_0 - S_2$
	6.1	5.94	$S_0 - S_3$
	6.9		$S_0 - S_4$

creasing the primary electron energy the intensity bands increases being in a more degree the band E=4.92 eV. It can be found from fig. 2 and 3 that for compound 1 the intensity ratio for bands 5.15 eV and 3.62 eV at E_0=20 eV is about 0.6, but at E_0=12 eV it is about 0.8. For compound 2 the intensity ratio of bands 4.92 eV and 3.39 eV varies in a more degree and is about 0.5 at E_0=20 eV and about 1.2 at E_0=12 eV.

The analysis of other electron energy loss spectra shows that in the region E_0=6.3 ... 14 eV the intensity of the second intensive band for these compounds is strongly increases and exceeds the intensity of the first intensive band.

To explain these peculiarities we used the results referred in a work[8] where the fluorescence excitation functions for some complex organic molecules are measured. For naphthalimide derivatives such dependences of excitation cross sections on electron energy are not measured yet, but their behaviour we can approximate with a sufficient accuracy to analyse.

All measured excitation functions have a rapid and smooth growth with the electron energy increase to maximum which is usually arranged in the region of three-four threshold energy of excitation of lowest singlet state S_1 and then a slow decrease in a wide region of electron energies takes place. There is a similar dependence of the excitation functions and cross sections for atoms[9].

For compound 2 the threshold excitation values of states S_1 and S_2 are about 2.5 and 4.5 eV accordingly, and then these functions reach their maxima at 7.5 and 13.5 eV. It can be assumed that the behaviour of these functions in the high energy region has the identical character. Since at E_0=20 eV the intensity ratio of bands 4.92 and 3.39 eV is about 0.5 (see above), then on the basis of our approximation this ratio at E_0=12 eV must be about 0.3.

The difference between the experimental and calculated intensity ratios of these bands at E_0=12 eV can be explained by summing up of energy losses of electrons due to excitation of triplet and singlet states in the band of E=4.92 eV. It is known that the cross sections of optically forbidden transitions excitation reach maxima at energies close to threshold and as a rule, the intensity of bands due to $S_0 - T_n$ transitions increases as E_0 decreases[1].

In this case it is unusual that electron energy losses connected with a populating of highlaying triplet state in the region of 4.92 eV are very strong and so, the differential cross section if excitation of optically forbidden and allowed transition is close to each other. This fact was discovered for the first time inspite of the many studied compounds of different classes.

ACKNOWLEDGMENT

This work was supported, in part, by a Soros Foundation Grant awarded by the American Physical Society.

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Date Received: August 4, 1993
Date Accepted: September 9, 1993