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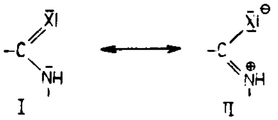
Thioamide and Selenoamide Bands in IR Spectra

Pasma tioamidowe i selenoamidowe w widmach IR

Тиоамидные и селеноамидные полосы в инфракрасных спектрах

Ureide and amide moieties are present in numerous compounds showing biological and pharmacological activity. Identification of these compounds as well as the products of their degradation is often required. One of the methods commonly used for this purpose is the comparative analysis of their infrared spectra. In IR spectra of compounds containing thioamide or thioureide groups characteristic absorption bands are always present. Therefore, the knowledge of their origin and localization in these spectra is of a great importance for analytical research.

In compounds containing ureide or amide moieties, in which the nitrogen atom is linked to the carbon atom of the $>C=X$: ($X=O$, S, Se) group, the strong electromeric effect occurs. In its consequence an increase of ionic form II contribution in the total molecular structure takes place:



I II

A comparative analysis of UV spectra of series of isologs of oxygen, sulfur and selenium various types of compounds containing ureide or amide moiety [16, 17, 23—25] confirm domination of the molecular structure II. In UV spectra of these isologs a strong bathochromic shift is observed in the series order from oxygen to sulfur to selenium containing compounds. This bathochromic shift can be explained either by destabilization of the structure I because of difficulty of π-bond formation with increasing interatomic distance or by stabilization of the structure II due to increased ability of the chalcogen atom to accept electrons. In both cases, the result is to decrease the energy difference between the states I and II and the shift of the absorption band to a longer wavelength. The measurements of dipole moments and dissociation constants [19, 23] confirm that the polarity of the $>$C=X bond increases in the order Se$>$S$>$O and the increase is weaker for the S$\rightarrow$Se substitution than for the S$\rightarrow$O replacement.

UV spectra, as shown above, make possible univocal determination of the chalcogen atom quality within the $>$C=X chromophore group present in the ureide or amide system. It is far more difficult to localize this group in the IR spectra. In compounds having the $-\mathrm{HN}-\overset{|}{\mathrm{C}}=\mathrm{X}$ (X=O, S, Se) group only the localization of νC=O band can be easily assigned (it is so called Amide I band). The C=S and C=Se bonds are weaker than the carbonyl bond and therefore absorb at lower frequencies where they are far more susceptible to coupling effects within the $-\mathrm{HN}-\overset{|}{\mathrm{C}}=\mathrm{X}$ system. The presence of the nitrogen atom influences the $>$C=X (X=S, Se) bond making its localization more labile. In other types of compounds in which carbon of the $>$C=X groups is linked to other than nitrogen atoms, the localization of the $>$C=X (X=S, Se) band makes no difficulty.

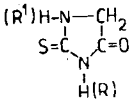
Numerous authors have attempted to localize absorption bands characteristic of the C=S group linked to the nitrogen atom within IR spectra of various nitrogen containing thiocarbonyl derivatives. They came, however, to divergent conclusions concerning localization of this group vibrations and the vibration character.

In particular, the IR spectra of thioureas were extensively studied. Randall et al. [29] first observed that a strong absorption band is present in the range 1613—1471 cm^{-1} which they assigned to C-N vibrations. Subsequently Ettlinger [11] localized C=S vibrations at the 1540 cm^{-1} frequency whereas Stewart [34] localized the same group vibrations at 1413 cm^{-1}. More detailed research for cyclic thioureides were carried out by Mecke et al. [26, 27]. They localized the C=S band in the range 1209—1201 cm^{-1} and found the occurrence of two amide bands called Amide II and Amide III bands, in the ranges 1565—1500 cm^{-1} and 1322—1273 cm^{-1}, respectively. Those vibrations were characterized as the result of coupling of the stretching vibrations (ν) of the C-N bond with the bending vibrations (δ) of the N-H bond. On the other hand Lane et al. [20] and Yamaguchi et al. [38] on the basis of their study of thiourea and N-methylthiourea had suggested more complex coupling between the νC-N and νC=S and correspondingly ρNH_2 and δNH vibrations. In result two composed bands appeared which were localized at 1417 and 1083 cm^{-1} and 1470 and 972 cm^{-1}. Besides of these bands these authors observed the presence of the Amide II and Amide III bands, as described by Mecke et al. [26, 27], and localized them at 1550 and 1296 cm^{-1}, respectively. The idea of the amide bands was confirmed by Rao and Venkataraghavan [30] in their research carried out on thioureas.

Alike for thioureas also IR spectra of thiosemicarbazides were analysed. First Bogomolov et al. [3] studied these compounds and reported strong absorption band in the range 1535—1500 cm^{-1}. Then Lieber et al. [21] localized the C=S band at 1395—1346 cm^{-1}, whereas absorption at 1548—1522 cm^{-1} assigned to vibrations of the C-N bond. Later Gingras et al. [12] showed that in spectra of a few thiosemicarbazones the νC=S vibrations give the absorption band in the range 1130—1010 cm^{-1}. At the same time Sadler [32] had localized the same band for aromatic thiosemicarbazones at 1378—1366 cm^{-1}.

In IR spectra of thioamides the localization of C=S band was for the first time assigned by Marvel et al. [22] to the range 1230—1180 cm^{-1} (for thiopropionamide and N-butylthioacetamide). The presence of Amide II and Amide III bands in IR spectra of thioamides, alike in the spectra of thioureas, was shown by Mecke et al. [26, 27]. They identified these bands at 1500 and 1290 cm^{-1}, respectively, in the spectra of thiolactams whereas the C=S group vibrations localized at 1120 cm^{-1}. On the ground of these results Hadzi [13] interpreted the tiobenzanilide and thiofuranilide spectra localizing the Amide II (1535—1520 cm^{-1}) and the Amide III (1375—1320 cm^{-1}) bands, but was unable to find any correlations for vibrations of the C=S group. Another interpretation was put forward by Davies and Jones [8]. They analysed IR spectra of thioformamide and suggested that the coupling of two C=S and C-N vibrations causes asymmetrical ν_aNCS vibrations giving the absorption band at 1443 cm^{-1} and symmetrical ν_sNCS vibrations at 1288 cm^{-1}. This interpretation was corrected by Rao and Venkataraghavan [30] who found in the thioacetamide spectra three bands resulting from the coupling of the stretching νC-N and νC=S vibrations with the δN-H deformation vibrations. In contrast to the above presented results there are two subsequent reports which localize the C=S vibrations. Spinner [33] suggested the range νC=S at 1180—1090 cm^{-1} in spectra of mercaptoazoaromatic derivatives and Bellamy [1] assigned the νC=S vibrations to 980 cm^{-1} frequency in the spectra of thioacetamide.

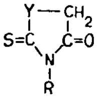
Localization of the C=S bond vibrations in IR spectra was extensively studied on more complicated structure than that of thioureas, thiosemicarbazides and thioamides. In particular they concerned heterocyclic rings comprising the thiourea and thioamide moieties. There were for example attempts to localize the C=S bond absorption in the IR spectra of 2-thiohydantoins but their results were in discrepancy: 1425—1400 cm^{-1} [28] and about 1200 cm^{-1} [10]. The study of Elmore [9] seem to be most exhaustive. He observed in the IR spectra of 2-thiohydantoins:



occurrence of the "thioureide" band, localization of which depends upon a substitution of nitrogen atoms. In thiohydantoins with non-substituted nitrogen atoms it is localized in the range 1562—1543 cm^{-1}, in the 2-thiohydantoins substituted on the one nitrogen atom in the range 1539—1508 cm^{-1} and in those substituted on the both nitrogen atoms in the range 1525—1458 cm^{-1}. From shifts of the bands resulting from the deuteration of these compounds Elmore [9] concluded that this "thioureide" band results from a coupling of the C-N stretching vibrations and the N-H bending vibrations. In the spectra of 2-thiohydantoins additional two other bands appeared (1400—1320 cm^{-1} and 1100—960 cm^{-1}) described as mixed vibrations of the $-HN-\overset{|}{C}=S$ group.

Rao [31] has reviewed similar observations made for other systems containing thioamide group. He suggested that in compounds in which the C=S group is linked to one or two nitrogen atoms localization of "pure" stretching vibrations of the C=S bond is impossible. In the thioamide moiety the stretching νC-N and νC=S vibrations and the deformation δN-H vibrations conjugate together which causes an appearance of characteristic bands. In these bands' structure the C=S group vibrations participate, most strongly in the bands at low frequency. Rao found that in IR spectra of the thioamide moiety containing compounds these bands are most often present at 1570—1395 cm^{-1}, 1420—1260 cm^{-1} and 1140—940 cm^{-1}. He called them the Ist, IInd and III rd "$-\overset{|}{N}-\overset{|}{C}=S$" bands, respectively. The above-presented interpretation was confirmed by Suzuki [35—37] in his study of thioamides. This author observed also the presence of the IVth "$-\overset{|}{N}-\overset{|}{C}=S$" band at 850—680 cm^{-1} which results from the mixed vibrations of the thioamide group.

Also Cogrossi [4] in his extensive study of IR spectra of numerous five-membered heterocyclic compounds of the type:



where Y=O, NH, S and Se

confirmed Rao's conclusions. In all these compounds Cogrossi observed the presence of four thioureide bands: I (1550—1300 cm^{-1}) described as ν_s(C-N-C)+δNH, II (1300—1200 cm^{-1}) assigned as ν_a(C-N-C), III (1180—1100 $^{-1}$) interpreted as mixed, with dominating contribution of $\nu C=S$ and IV (900—860 cm^{-1}).

As shown above, controversial problem of the localization and interpretation of the C=S band was solved by showing participation of $\nu C=S$ vibrations in the structure of thioamide bands present in IR spectra of compounds containing the thioureide moiety. Nevertheless, though at present localization of the thioamide bands in IR spectra makes no difficulty, the interpretation of particular vibrations is often still unequivocal. Results of research carried out on thioureas, thiosemicarbazides and thioamides have been analysed in detail because they present a point of reference for research concerning localization of the C=Se bond vibrations in IR spectra of the compounds containing the selenoamide group. Such research is rather non-numerous and concerns mostly selenoisologs of the above discussed compounds. There is almost entire lack of reports concerning a localization of the $\nu C=Se$ vibrations in IR spectra of the heterocyclic compounds having the $-HN-\overset{|}{C}=Se$ group. Comparison of results is additionally difficult because of a lack of commonly accepted terminology. Various authors use different terms for the same bands. This one could already notice in the literature of thiocarbonyl compounds but it occurs even more distinctly in the papers concerning their seleno-isologs.

First attempts to localize vibrations of the C=Se bond present within the $-HN-\overset{|}{C}=Se$ group were those of Collard-Charon and Renson. In 1963 in the series of papers they analysed IR spectra of selenoureas [5], selenosemicarbazides [6] and selenoamides [7] and compared them with spectra of the corresponding thioisologs. On the basis of band shifts which resulted from deuterization and methylation of the studied compounds they observed an occurrence of two bands in all tested compounds: Amide II (1550—1500 cm^{-1}) and Amide III (1300—1240 cm^{-1}), originating from coupling of the νC-N and δN-H vibrations. What more, they assigned some of the bands to the stretching vibrations of the C=Se bond, earlier expecting that this band should appear near the C=S band i.e. in the range 1200—950 cm^{-1}. From UV spectra selenoureas (λ_{max}=259—261 nm), selenosemicarbazides (λ_{max}=253—265 nm) and selenoamides (λ_{max}=290—298 nm) these authors concluded that for selenoamides the C=Se band should be localized at the lowest wave numbers. The results obtained confirmed their conclusions. A localization of the C=S and C=Se bands changed a little depending upon a degree of the nitrogen atom substitution but the difference in these two bands position never exceeded 10 cm^{-1} (for example: for N-n-butylthiourea — 1115 cm^{-1} and for N-n-butylselenourea — 1110 cm^{-1}). On the ground of an extensive analysis of numerous spectra the C=Se band was localized in the range 1115—1080 cm^{-1} for selenoureas, at 1075—990 cm^{-1} for selenosemicarbazides and at 1100—950 cm^{-1} for selenoamides. In general, the νC=Se band occurred at slightly lower frequencies than the νC=S band what stems from stronger polarization of the C=Se bond. The spectra of thio- and selenoureas contained a lower number of bands and were more easily interpreted than those of selenosemicarbazides and, in particular, of selenoamides. Finally in many cases the interpretation was unclear and indefinite. Following Collard-Charon and Renson [5—7], Bergmann et al. [2] assigned to the C=Se vibrations a band at 1140—1138 cm^{-1} in IR spectra of 5.5-disubstituted 2-selenohydantoins.

Subsequently Jensen and Nielsen [15] analysed and interpreted IR spectra of about 150 thioamides, selenoamides, thioureas and selenoureas. In those spectra they observed seven characteristic bands, and termed them the thioamide A, B, ... G bands. Each of these bands behaved in a characteristic way when the compounds were deuterated, S- or Se-alkylated, or transformed into metal complexes. The A and E bands were present only in the spectra of primary thioamides, i.e. their occurrence was associated with the presence of the NH_2 group. Jensen and Nielsen [15] found that the IR spectra of thio- and selenoisologs studied were identical up to the wavelength of 800 cm^{-1}. Only in the range 800—600 cm^{-1} (the band G) some significant differences were observed. On substitution of sulfur with selenium this band was shifted 30—100 cm^{-1} towards lower frequencies. Since the range 800—600 cm^{-1} is usually cited for stretching vibrations of the C-S single bond, Jensen and Nielsen [15] concluded that the C=S vibrations have a dominating character of the C-S single bond vibrations and hence they are localized in this range. The same suggestion can be extended to selenoamides in the C=Se vibrations which are present at lower frequencies.

Hallam and Jones [14] reviewed works of Collard-Charon and Renson [5—7] and Jensen and Nielsen [15] and studied themselves IR spectra of thio- and selenolactams $\overline{(\mathrm{CH_2})_n\text{—CX—NH}}$ where X=S, Se and $n=3, 4, 5, 7$ and 11. Also in these spectra the striking similarity was noticed for the compounds with a small ring ($n \leqq 7$). The suggested interpretation concerned the range 1400—550 cm^{-1}. Though in some points unequivocal, it correlates with some earlier assignments of localization or participation of the C=S and C=Se vibrations. In particular, in the compounds where $n=3$ and 4 the $\nu C=X$ vibrations according to Hallam and Jones [14] can be localized at 1115 cm^{-1} (S) and 1085 cm^{-1} (Se), what corresponds with earlier conclusions of Mecke et al. [26, 27] for the $\nu C=S$ vibrations and of Collard-Charon and Renson [5—7] for the $\nu C=S$ and $\nu C=Se$ vibrations. In the compounds, where $n>4$ such a localization is impossible. In IR spectra of the studied lactams Hallam and Jones [14] could not confirm the correlations for the G band suggested by Jensen and Nielsen [15] what could support the assignment to this band a character of the C-S or C-Se single bond vibrations. They suggested therefore that the G band features are due to the in-plane deformation of the $-\overset{|}{N}-\overset{|}{C}=X$ group, and this deformation would be expected to be sensitive to the mass and chemical nature of the X atom.

In the literature there is a lack of data concerning comparative analysis and localization of the thioamide and selenoamide bands in IR spectra of more complex compounds. On the basis of the above discussed data concerning more simple compounds such an attempt was recently made [16, 17] for 3.5-disubstituted hydantoins, 2-thiohydantoins and 2-selenohydantoins. The IR spectra of these compounds appeared to be far more complex than those of thio- and selenoureas and thio- and selenoamides. The analysis concerned only the range 4000—900 cm^{-1} since in the longer wavelengths the spectra were too complex for localization of the discussed groups. In the range 3000—1000 cm^{-1} the spectra of all the studied compounds were similar. They showed strong absorption bands at the ranges 1600—1400 cm^{-1}, 1300—1200 cm^{-1} and 1200—1000 cm^{-1}, which corresponded to the coupled vibrations within the $-HN-\overset{|}{C}=X$ group, as described in the literature. The introduction to these compounds of the O, S or Se atom as X did not change significantly these bands' positions. This suggests that the participation of the $C=X$ group vibrations in these bands is negligible and these bands results from coupling of the C-N stretching vibrations with the N-H deforming vibrations with the dominating influence of the first or second ones.

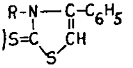
In the majority of 2-thiohydantoin derivatives the weak band occurred in the range 1000—990 cm^{-1} whereas in 2-selenohydantoins the band of similar intensity was localized in the range 960—945 cm^{-1}. Because of these bands' localization and the difference in their wavenumbers it was hypothesized that the band at 1000—990 cm^{-1} results from the mixed vibrations of the $-HN-\overset{|}{C}=S$ group with the dominating contribution of the $\nu C=S$ vibrations and the band at 960—945 cm^{-1} results

Table 1. Localization of thioamide and selenoamide bands in IR spectra (X=S, Se)

Author /Year/	Rao /1962/	Suzuki /1962/	Collard–Charon and Renson /1963/	Jensen and Nielsen /1966/	Hallam and Jones /1969/	Cogrossi /1972/	Korohoda /1980–1983/
Band	I $-\overset{\vert}{N}-\overset{\vert}{C}=S$		Amide II	B		Thioureide I	Thio/seleno/amide I
Range /cm^{-1}/	1570–1395		1550–1500	1600–1400		1550–1300	1600–1400
Assignment			δ_1NH/νC$\overset{\cdots}{=}$N	ν_sNCX$\approx\nu$C$\overset{\cdots}{=}$N		ν_s/C–N–C/δNH	ν_sNCX $\approx$ νC$\overset{\cdots}{=}$N
Band	II $-\overset{\vert}{N}-\overset{\vert}{C}=S$		Amide III	C		Thioureide II	Thio/seleno/amide II
Range /cm^{-1}/	1420–1260		1300–1240	1400–1200		1300–1200	1300–1200
Assignment			νC$\overset{\cdots}{=}$N/δ_1NH	νCN/NH		ν_s/C–N–C/	νCN/NH
Band	III $-\overset{\vert}{N}-\overset{\vert}{C}=S$			D		Thioureide III	Thio/seleno/amide III
Range /cm^{-1}/	1140–940		1110–965	1200–1000	1115–1085	1180–1100	1200–1000
Assignment			νC=X	ν_sNCX/NH	ν_sNCX/δ_1NH$\approx\nu$C=X	mixed, νC=S	ν_s NCX/NH, νC=X
Band		IV $-\overset{\vert}{N}-\overset{\vert}{C}=S$		G		Thioureide IV	Thio/seleno/amide IV
Range /cm^{-1}/		850–680		800–600		900–860	990–890
Assignment				νC–X	δ_1NCX	mixed	mixed, νC=X

from the mixed vibrations of the $-\mathrm{HN}-\overset{|}{\mathrm{C}}=\mathrm{Se}$ group with domination of the $\nu\mathrm{C}=\mathrm{Se}$ vibrations.

Recently an attempt was made [18] to localize also the thio- and selenoamide bands in the thiazoline derivatives of the type:



In a series of 4-thiazoline-2-thiones and 4-thiazoline-2-selenones the thio- and selenoamide bands in IR spectra were observed in the ranges: the Ist band: 1510—1480 cm^{-1}, the IInd band: 1310—1220 cm^{-1}, and the IIIrd band: 1120—1040 cm^{-1}. In the Ist and IInd thio- and selenoamide bands contribution of the C=S and C=Se stretching vibrations is minimal. In the IIIrd band this contribution is significant because in the spectra of 4-thiazoline-2-selenones this bands is shifted 10—30 cm^{-1} toward lower wavenumbers in relation to the same band of isologic 4-thiazoline-2-thiones. Moreover, in the spectra of the discussed compounds there is a strong band at 940—890 cm^{-1}, which can be described as the IVth thio- and selenoamide band. This interpretation is supported by the absence of this band in compounds in which sulfur or selenium atoms are replaced by the R-imine group.

Most significant of the above described results and assignments are collected in the Table 1.

The data presented in this short review concern the problem of localization of the thio- and selenoamide bands in IR spectra of rather simple compounds. Nevertheless, they can be used as a reference point for an interpretation of IR spectra of compounds characterized by a more complex structure.

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STRESZCZENIE

Przedstawiono przegląd badań dotyczących lokalizacji pasm tioamidowych i selenoamidowych w widmach IR. Dokonano analizy interpretacji tych pasm pod kątem udziału drgań wiązania $>C=X$ ($X=S$, Se) w strukturze widma.

РЕЗЮМЕ

В данной работе представлены результаты исследований о расположении тиоамидных и селеноамидных полос в инфракрасных спектрах. Проведено анализ интерпретации этих полос в смысле участия колебаний связи $>C=X$ ($X=S$, Se) в структуре спектра.