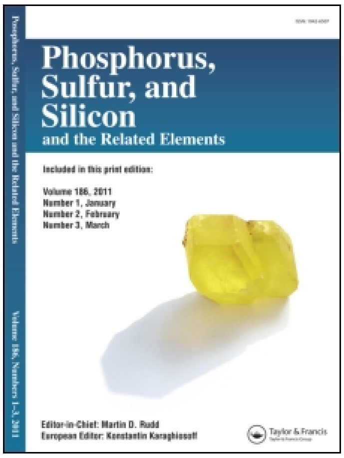

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MAXIMUM BOND ORDER HYBRID ORBITAL CALCULATIONS OF THE S=O STRETCHING FREQUENCIES FOR SULPHURYL AND THIONYL COMPOUNDS

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A new generalized relationship, which includes the contributions of the net atomic charges and the orbital characters of the hybrid atomic orbitals forming the S=O bond, is employed to elucidate the S=O bond stretching vibrational frequencies based on the maximum bond order hybrid orbital calculations. The S=O stretching frequencies calculated by using the explicit relationship obtained are in good agreement with the corresponding experimental frequencies.

Keywords: orbital calculations; atomic orbitals; bond stretching; bonal order; S=O bond

INTRODUCTION

As is well-known, the view of the variable character of S=O bond was concluded primarily from the systematic comparisons of physical and chemical properties of sulfoxides (R_1-SO-R_2) and sulfones (R_1-SO_2-R_2), such as the S=O bond lengths, bond orders, bond stretching vibrational frequencies and force constants.[1–22] It was reported that the S=O stretching frequency (or the corresponding force constant) and S=O bond order both increase with the increasing electronegativities of the group R_1 and

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R_2 in the sulfones[22] and, therefore, Gillespie and Robinson established a simple linear relationship,[22]

$$n = 1.11 \times 10^{-6}k + 0.7 \qquad (1)$$

to evaluate the bond order *n* from the use of the force constant *k* for the S=O stretching vibration.

The IR spectra of organic sulfones show two strong absorption bands at 1260–1310 cm^{-1} and at 1110–1160 cm^{-1} associated with the symmetric and asymmetric stretching vibrations of the two S=O bonds, respectively.[23] Ever since the pioneering work by Koch and co-workers,[24] there has persisted a tendency to average the two stretching frequencies, such as by using the "average rule" pointed out by Lehmann.[25] However, later many observations and comparisons indicated that the changes of the symmetric stretching frequency provide more valuable structural information of the series of molecules.[1]

With the increasing number of these compounds for which their experimental spectroscopic data have been reported, many researchers attempted to correlate the frequencies of infrared absorption bands with specific structural characters. Over thirty years ago, Gillespie and Robinson proposed an empirical relationship between the S=O bend length and stretching frequencies in sulphuryl and thionyl compounds,[22]

$$log\nu_{SO} = -3.7log\ r_{SO} + 3.68 \qquad (2)$$

where r_{SO} is the S=O bond length, and v_{SO} is the root mean square of the symmetric and asymmetric stretching frequencies of the S=O bond. Ten years later, the explicit relationships were given separately for the two kinds of stretching frequencies by Brunvoll and Hargittai.[26] These explicit relationships indicate that the standard deviation corresponding to the symmetric stretching frequency is lower than that corresponding to the asymmetric stretching frequency. However, the established relationships are useful only for discussing the change of the stretching frequencies in the series of molecules.[26] At the same time, many attempts have been made to derive a set of semiempirical correction factors for the computed frequencies.[25, 27–38] Different correction factors were used for different vibrational mode rather than general correction factors for all modes or groups of modes.

It is the main objective of this paper to establish a new generalized relationship for calculating the S=O stretching vibrational frequencies, as an extension of our recently proposed generalized relationship for calculating nuclear spin-spin coupling constants.

In our previous work, a novel relationship[39] was introduced through a theoretical consideration of the Fermi contact mechanism of nuclear spin-spin coupling to calculate the nuclear spin-spin coupling constants for the atom pairs for which the Fermi contact mechanism is dominant.[40,41] Based on this relationship and a linear relationship between the bond stretching frequencies and the coupling constants, a simple relationship,[42] which includes contributions of the *s*-characters of the hybrid orbitals and the net atomic charges, was introduced to calculate the bond stretching frequencies:

$$\begin{aligned}\nu_{\mathrm{AB}} = {} & K_{\mathrm{AB}}(s\%)_{\mathrm{A}}(s\%)_{\mathrm{B}} + K_{Q\mathrm{A}}Q_{\mathrm{A}}(s\%)_{\mathrm{A}} + \\ & K_{Q\mathrm{B}}Q_{\mathrm{B}}(s\%)_{\mathrm{B}} + K_{\mathrm{A}}(s\%)_{\mathrm{A}} + K_{\mathrm{B}}(s\%)_{\mathrm{B}} + C_{\mathrm{AB}} \qquad (3)\end{aligned}$$

Here Q_{A} and Q_{B} are the net charges of atoms A and B, respectively. This relationship has been employed, together with the maximum bond order hybrid orbital (MBOHO) method,[43] to successfully elucidate C-H and P=S stretching frequencies.[42,44] Recently, based on a further theoretical analysis of the Fermi contact and non-contact terms in the Ramsey theory of nuclear coupling constants, a more generalized semiempirical relationship has been derived for calculating nuclear spin-spin coupling constants: [45]

$$\begin{aligned}J_{\mathrm{AB}} = {} & \sum_{i=0}^{l_{\max}^{\mathrm{A}}-1}\sum_{j=0}^{l_{\max}^{\mathrm{B}}-1} k_{ij\mathrm{AB}}W_{i\mathrm{A}}W_{j\mathrm{B}} + \sum_{l=0}^{l_{\max}^{\mathrm{A}}-1} k_{lQ\mathrm{A}}Q_{\mathrm{A}}W_{l\mathrm{A}} + \sum_{l=0}^{l_{\max}^{\mathrm{A}}-1} k_{l\mathrm{A}}W_{l\mathrm{A}} \\ & + \sum_{l=0}^{l_{\max}^{\mathrm{B}}-1} k_{lQ\mathrm{B}}Q_{\mathrm{B}}W_{l\mathrm{B}} + \sum_{l=0}^{l_{\max}^{\mathrm{B}}-1} k_{l\mathrm{B}}W_{l\mathrm{B}} + k_{\mathrm{EA}}Q_{\mathrm{A}} + k_{\mathrm{EB}}Q_{\mathrm{B}} + c_{\mathrm{AB}} \qquad (4)\end{aligned}$$

where $l_{\max}^{\mathrm{A}}$ and $l_{\max}^{\mathrm{B}}$ are the maximum angular momentum numbers of the valence orbitals of atoms A and B, respectively. Q_{A} and Q_{B} are the net charges of atoms A and B, respectively. W_{iA} and W_{iB} are *s*-characters of the atomic orbitals associated with the angular momentum quantum number $l=i$ in the hybrid orbitals $\emptyset_{\mathrm{A}}$ and $\emptyset_{\mathrm{B}}$ belonging to atoms A and B, respectively. Thus, $W_{0\mathrm{A}}\equiv(s\%)_{\mathrm{A}}$ and $W_{0\mathrm{B}}\equiv(s\%)_{\mathrm{B}}$, $W_{1\mathrm{A}}\equiv(p\%)_{\mathrm{A}}$ and $W_{1\mathrm{B}}\equiv(p\%)_{\mathrm{B}}$ *etc.*. These quantities can be evaluated by use of our MBOHO procedure.[43] Besides, $k_{ij\mathrm{AB}}$, $k_{l\mathrm{QA}}$, $k_{l\mathrm{A}}$, $k_{l\mathrm{QB}}$, $k_{l\mathrm{B}}$, k_{EA}, k_{EB} and c_{AB} are independent parameters which are constants for the same kind of chemical bond.

As we know, there is a good linear relationship between the bond stretching vibrational frequencies and the corresponding nuclear spin-spin coupling constants of C-H bonds.[42,46] If this simple linear relationship is extended to a general chemical bond A-B, then we may have

$$\nu_{\mathrm{AB}} = aJ_{\mathrm{AB}} + b. \tag{5}$$

Substitution of Eq.(4) into Eq.(5) gives

$$\nu_{\mathrm{AB}} = \sum_{i=0}^{l_{\max}^{\mathrm{A}}-1} \sum_{j=0}^{l_{\max}^{\mathrm{B}}-1} K_{ij\mathrm{AB}} W_{i\mathrm{A}} W_{j\mathrm{B}} + \sum_{l=0}^{l_{\max}^{\mathrm{A}}-1} K_{lQ\mathrm{A}} Q_{\mathrm{A}} W_{l\mathrm{A}} + \sum_{l=0}^{l_{\max}^{\mathrm{A}}-1} K_{l\mathrm{A}} W_{l\mathrm{A}}$$
$$+ \sum_{l=0}^{l_{\max}^{\mathrm{B}}-1} K_{lQ\mathrm{B}} Q_{\mathrm{B}} W_{l\mathrm{B}} + \sum_{l=0}^{l_{\max}^{\mathrm{B}}-1} K_{l\mathrm{B}} W_{l\mathrm{B}} + K_{\mathrm{EA}} Q_{\mathrm{A}} + K_{\mathrm{EB}} Q_{\mathrm{B}} + C_{\mathrm{AB}} \tag{6}$$

where $K_{ij\mathrm{AB}} = ak_{ij\mathrm{AB}}$, $K_{lQ\mathrm{A}} = ak_{lQ\mathrm{A}}$, $K_{l\mathrm{A}} = ak_{l\mathrm{A}}$, $K_{lQ\mathrm{B}} = ak_{lQ\mathrm{B}}$, $K_{l\mathrm{B}} = ak_{l\mathrm{B}}$, $K_{\mathrm{EA}} = ak_{\mathrm{EA}}$, $K_{\mathrm{EB}} = ak_{\mathrm{EB}}$ and $C_{\mathrm{AB}} = ac_{\mathrm{AB}} + b$. Obviously, $K_{ij\mathrm{AB}}$, $K_{lQ\mathrm{A}}$, $K_{l\mathrm{A}}$, $K_{lQ\mathrm{B}}$, $K_{l\mathrm{B}}$, K_{EA}, K_{EB} and C_{AB} become independent parameters which are constants for the same kind of chemical bond. Equation (6) may be regarded as a generalized parameterized relationship for calculating stretching vibrational frequencies of A-B bonds. This parameterized relationship is employed, in this paper, to elucidate the S=O bond stretching frequencies. For the case of S=O bond, $l_{\max}^{\mathrm{S}} = 2$ and $l_{\max}^{\mathrm{O}} = 1$, Eq. (6) becomes

$$\nu_{\mathrm{S=O}} = K_{00\mathrm{SO}}(s\%)_{\mathrm{S}}(s\%)_{\mathrm{O}} + K_{0\mathrm{QS}}Q_{\mathrm{S}}(s\%)_{\mathrm{S}} + K_{0\mathrm{QO}}Q_{\mathrm{O}}(s\%)_{\mathrm{O}}$$
$$+K_{0\mathrm{S}}(s\%)_{\mathrm{S}} + K_{0\mathrm{O}}(s\%)_{\mathrm{O}} + K_{\mathrm{ES}}Q_{\mathrm{S}} + K_{\mathrm{EO}}Q_{\mathrm{O}} + K_{10\mathrm{SO}}(p\%)_{\mathrm{S}}(s\%)_{\mathrm{O}}$$
$$+K_{1\mathrm{QS}}Q_{\mathrm{S}}(p\%)_{\mathrm{S}} + K_{1\mathrm{S}}(p\%)_{\mathrm{S}} + C_{\mathrm{SO}} \ . \tag{7}$$

CALCULATION METHOD

The MBOHO calculation has been carried out for a number of organic sulfur compounds. For a given molecule, before the MBOHO calculation we must determine molecular geometry and calculate the corresponding one-electron density matrix. As we know, the MNDO method presented by Dewar *et al.*[47-49] is qualified for geometry optimization of the molecules containing sulfur atom even if the *d* orbitals are not included in the calculation. However, the density matrix obtained from the MNDO calculation without *d* orbitals cannot be used to construct the MBOHOs containing hybridization of *d* orbitals. In the present work, we employed the MNDO method to optimize geometries of all the molecules considered, and because the *d* orbitals are not involved in our MNDO calculations the optimized geometries were employed to perform the extended Hückel molecular orbital (EHMO)[47] calculations involving *d* orbitals of sulfur atom. The density matrix obtained from the EHMO calculation was used to carry out the MBOHO calculation and to evaluate the net atomic charges based on Mulliken population analysis.

All the parameters used in the MNDO calculations were reported in literature,[48-50] and all the parameters used to perform the EHMO calculation are the default values in the EHMO program.[47]

RESULTS AND DISCUSSION

The *s*-characters of S and O atoms, *p*-character of S atom and net charges of S and O atoms are summarized in Table I. For each sulphuryl compound, listed in Table I are the average values for the two S=O bonds because we concern with the symmetric stretching vibrational frequencies reported. Based on these numerical values, the least-squares procedure of the theoretically calculated S=O stretching frequencies versus the experimental frequencies given in the literature[1] is performed to determine the parameters in Eq.(7). Thus, we obtain the following explicit relationship:

$$\begin{aligned}\nu_{\mathrm{S=O}} = {} & 3.261(s\%)_{\mathrm{S}}(s\%)_{\mathrm{O}} + 7.959(s\%)_{\mathrm{S}}Q_{\mathrm{S}} - 410.208(s\%)_{\mathrm{O}}Q_{\mathrm{O}} \\ & -215.156(s\%)_{\mathrm{S}} - 475.156(s\%)_{\mathrm{O}} - 522.828Q_{\mathrm{S}} \\ & +24197.641Q_{\mathrm{O}} + 0.200(s\%)_{\mathrm{O}}(p\%)_{\mathrm{S}} + 6.562Q_{\mathrm{S}}(p\%)_{\mathrm{S}} \\ & -27.029(p\%)_{\mathrm{S}} + 30574.762(\mathrm{cm}^{-1}) \qquad (8)\end{aligned}$$

with a correlation coefficient of 0.98 and a standard deviation of 11.5 cm^{-1}. Besides, if we ignore the contribution of the change of *p*-character of S atom to the S=O bond stretching frequency, then the total number of independent parameters to be calibrated is reduced from 11 to 8. Meanwhile, the standard deviation becomes 16.0 cm^{-1}. It follows that the change of the *p*-character of S atom is significant for describing the change of the S=O bond stretching frequency.

The S=O bond stretching vibrational frequencies calculated by Eq.(8) are all listed in Table I compared with the corresponding experimental frequencies. A survey of the data in Table I reveals that the calculated S=O stretching frequencies are, on the whole, in good agreement with the experimental results. Many important trends of the experimental frequencies are reasonably reproduced. Illustrated as follows are the most important trends discussed by Szmant.[1]

TABLE I The calculated orbital characters of MBOHOs, net atomic charges and S=O bond stretching vibrational frequencies compared with the experimental frequencies[a] (in cm^{-1})

	(s%)s	*(s%)o*	*(p%)s*	*Qs*	*Qo*	*Expt.*	*Calc.*
$CH_3SO_2CH_3$	23.64	55.52	62.30	1.7100	−0.9670	1152	1146
$CH_3SO_2CH_2CH_3$	23.33	55.82	62.21	1.6460	−0.9720	1144	1144
$CH_3SO_2CH_2CH_2CH_3$	23.62	55.65	62.17	1.6920	−0.9730	1141	1148
$CH_3SOCH(CH_3)_2$	23.66	55.61	62.07	1.6940	−0.9710	1142	1135
$CH_3SO_2(CH_2)_3CH_3$	23.69	55.69	62.17	1.6810	−0.9760	1141	1147
$CH_3SO_2C(CH_3)_3$	23.88	55.72	61.24	1.6710	−0.9740	1122	1138
$CH_3SO_2CHCH_2$	23.62	55.65	62.36	1.6910	−0.9720	1141	1141
$CH_3SO_2NH_2$	24.66	57.47	60.92	1.7760	−0.9550	1169	1171
CH_3SO_2OH	25.68	56.49	60.02	1.9510	−0.9370	1174	1183
CH_3SO_2Cl	25.45	57.25	60.31	1.8520	−0.9180	1175	1192
CH_3SO_2F	26.35	56.74	59.81	2.2080	−0.9120	1210	1219
$CH_3CH_2SO_2CH_2CH_3$	23.93	55.64	62.04	1.6740	−0.9660	1138	1139
$(CH_3CH_2CH_2)_2SO_2$	23.86	55.74	61.90	1.6690	−0.9630	1136	1146
$C(CH_3)_3)_2SO_2$	24.10	55.95	60.94	1.6140	−0.9850	1102	1120
$CH_2CHSO_2CHCH_2$	23.00	56.20	61.99	1.5880	−0.9740	1153	1151
$NH_2SO_2NH_2$	25.58	57.26	59.40	1.8390	−0.9450	1163	1176
$CH_3OSO_2OCH_3$	28.20	57.50	57.33	2.1760	−0.9050	1206	1198
$HOSO_2OH$	28.16	57.22	57.20	2.1660	−0.9000	1195	1200
SCl_2O_2	26.61	58.57	58.22	1.9920	−0.8970	1182	1194
SO_2F_2	29.70	56.91	57.02	2.7090	−0.8590	1269	1268
$C_6H_5SO_2C_6H_5$	22.80	56.58	61.69	1.5600	−0.9910	1161	1144
$C_6H_5SO_2CHCH_2$	22.97	56.24	62.10	1.5740	−0.9840	1153	1132
$C_6H_5SO_2NH_2$	24.20	56.73	60.76	1.7110	−0.9680	1167	1153
$C_6H_5SO_2F$	25.77	57.19	59.59	2.1130	−0.9310	1213	1198
$C_6H_5SO_2OH$	25.20	57.04	59.78	1.8640	−0.9520	1182	1173
$ClSO_2CCl_3$	26.12	57.64	57.67	1.9020	−0.9060	1183	1186
$ClSO_2CF_3$	26.26	57.36	60.36	1.7760	−0.8860	1239	1198
$ClSO_2OCH_3$	27.34	58.26	57.72	2.0810	−0.9020	1190	1202
$ClSO_2OH$	27.35	58.03	57.73	2.0790	−0.8960	1209	1204
$ClSO_2F$	27.92	57.93	57.63	2.3490	−0.8850	1228	1225
$FOSO_2F$	29.66	57.11	57.17	2.4790	−0.8510	1248	1249
$HOSO_2F$	29.95	57.14	57.12	2.4290	−0.8760	1230	1231

	(s%)s	(s%)o	(p%)s	Qs	Qo	Expt.	Calc.
CH_3OSO_2F	28.91	57.27	57.25	2.4350	−0.8820	1235	1231
CF_3SO_2F	27.52	56.73	59.83	2.1530	−0.8700	1240	1234
$CF_3SO_2NH_2$	25.75	56.48	60.90	1.7020	−0.9120	1200	1181
CH_3SOCH_3	21.61	52.78	68.72	0.6670	−0.9580	1072	1058
CH_3SOOCH_3	23.14	54.01	67.26	0.9350	−0.9070	1147	1158
$CH_3CH_2SOCH_2CH_3$	22.06	52.91	68.52	0.6280	−0.9500	1066	1065
$(CH_3CH_3CH_2)_2SO$	22.01	53.03	68.45	0.6190	−0.9530	1058	1057
$((CH_3)_2CH)_2SO$	22.24	55.66	67.95	0.6060	−0.9540	1053	1054
$C_6H_5SOC_6H_5$	21.24	54.90	67.14	0.5140	−0.9710	1052	1059
SOF_2	24.58	55.69	65.90	1.8010	−0.8270	1308	1311
$SOCl_2$	25.50	57.58	64.38	1.8090	−0.8140	1229	1234

[a]All the experimental frequencies come from Ref. [1].

1. The S=O stretching frequency increases with increasing the electronegativities of the substituents attached to the S atom. This can be seen from following examples:

(1) $F\text{-}SO_2\text{-}F$ $F\text{-}SO_2\text{-}OF$ $F\text{-}SO_2\text{-}CF_3$ $F\text{-}SO_2\text{-}OH$ $F\text{-}SO_2\text{-}Cl$ $F\text{-}SO_2\text{-}CH_3$
1269/1268 > 1248/1249 > 1240/1234 > 1230/1231 > 1228/1225 > 1210/1219

(2) $Cl\text{-}SO_2\text{-}F$ $Cl\text{-}SO_2\text{-}OH$ $Cl\text{-}SO_2\text{-}OCH_3$ $Cl\text{-}SO_2\text{-}CCl_3$
1228/1225 > 1209/1204 > 1190/1202 > 1183/1186

(3) $CH_3\text{-}SO_2\text{-}F$ $CH_3\text{-}SO_2\text{-}Cl$ $CH_3\text{-}SO_2\text{-}OH$ $CH_3\text{-}SO_2\text{-}NH_2$ $CH_3\text{-}SO_2\text{-}CH_3$ (cont'd)
1210/1219 > 1175/1192 > 1174/1183 > 1169/1171 > 1152/1146 >
$CH_3\text{-}SO_2\text{-}CH2CH_3$ $CH_3\text{-}SO_2\text{-}CHCH_2$
1144/1144 > 1141/1141

(4) SOF_2 $SOCl_2$ $SO(CH_3)_2$ SO_2F_2 SO_2Cl_2 $SO_2(CH_3)_2$
1308/1311 > 1229/1234 > 1072/1058 ; 1269/1268 > 1182/1194 > 1152/1146

Note that here, and below, the values under each molecular formula are always the experimental/calculated frequencies.

2. Substituents being capable of both inductive and resonance effects, when these two effects are in opposed direction, are primarily in accord with their inductive effects. For example,

$C_6H_5\text{-}SO_2\text{-}F$ $C_6H_5\text{-}SO_2\text{-}OH$ $C_6H_5\text{-}SO_2\text{-}NH_2$ $C_6H_5\text{-}SO_2\text{-}C_6H_5$ $C_6H_5\text{-}SO_2\text{-}CHCH_2$
1213/1186 > 1182/1173 > 1167/1153 > 1161/1144 > 1153/1132

3. An increase in the bulk of substituents tends to reduce the corresponding stretching frequency, such as:

(1)	CH_3-SO_2-CH_3		CH_3-SO_2-CH_2CH_3		CH_3-SO_2-$CH(CH_3)_2$
	1152/1146	>	1144/1144	>	1142/1135
(2)	CH_3-SO_2-CH_3		CH_3CH_2-SO_2-CH_2CH_3		$(C(CH_3)_3)_2SO_2$
	1152/1146	>	1138/1139	>	1102/1120

4. Additional terminal oxygen atoms tend to lower the corresponding stretching frequency when the electron-withdrawing substituents are present, while the opposite is true when the substituents are electron-donating. This can be also supported by some examples:

(1)	SO_2F_2		SOF_2
	1269/1268	<	1308/1311
(2)	SO_2Cl_2		$SOCl_2$
	1182/1194	<	1229/1234
(3)	CH_3-SO_2-CH_3		CH_3-SO-CH_3
	1152/1146	>	1072/1058
(4)	CH_3CH_2-SO_2-CH_2CH_3		CH_3CH_2-SO-CH_2CH_3
	1138/1139	>	1066/1065
(5)	$(CH_3CH_2CH_2)_2SO_2$		$(CH_3CH_2CH_2)_2SO$
	1136/1146	>	1058/1057
(6)	C_6H_5-SO_2-C_6H_5		C_6H_5-SO-C_6H_5
	1161/1144	>	1052/1059

It follows that the explicit relationship Eq.(8) obtained in this work is quite satisfactory for calculating the S=O bond stretching vibrational frequencies.

References

[1] H. H. Szmant, in *Sulfur in Organic and Inorganic Chemistry*, Ed. by A. Senning, Vol. 1 (Dekker, New York, 1971) p107.

[2] T. Birchall and R. J. Gillespie, Spectrochim. Acta 22, 681 (1966).

[3] N. Leonard and C. Johnson, J. Am. Chem. Soc. 84, 3700 (1962).

[4] C. Kraebel, S. Davis and M. Landon, Spectrochim. Acta 23A, 2541 (1967).

[5] G. Geiseler, J. Fruwert and F. Gyalogy, Spectrochim. Acta 22, 1165 (1966).
[6] W. R. Feairheller and J. E. Katon, Spectrochim. Acta 20, 1099 (1964).
[7] J. R. Shelton and K. E. Davis, J. Am. Chem. Soc. 89, 718 (1967).
[8] E. A. Robinson, Can. J. Chem. 39, 247 (1961).
[9] L. A. Carpino and L. V. McAdams, J. Am. Chem. Soc. 89, 5804 (1968).
[10] A. V. Jones, J. Chem. Phys. 18. 1263 (1950).
[11] G. Tosilini, Chem. Ber. 94, 2731 (1961).
[12] G. Kresze and A. Maschke, Chem. Ber. 94, 450 (1961).
[13] J. Chatt and D. M. P. Mingos, J. Chem. Soc. (A) 1770 (1969).
[14] T. Gramstad, Spectrochim. Acta 19, 829 (1963).
[15] S. D. Ross, Spectrochim. Acta 18, 1575 (1962).
[16] J. C. Kice and K. Ikura, J. Am. Chem. Soc. 90, 7378 (1967).
[17] H. H. Szmant and W. Emerson, J. Am. Chem. Soc. 78, 454 (1956).
[18] A. J. Banister, L. F. Moore and J. S. Padley, Spectrochim. Acta 23A, 2705 (1967).
[19] C. C. Price and S. Oae, Sulfur Bonding 77, 82 (1962).
[20] A. Beaman and R. Robins, J. Am. Chem. Soc. 83, 4038 (1961).
[21] Y. A. Kolesnik and V. V. Kozlov, Russ. Chem. Rev. (Engl. Transl.) 37, 519 (1968).
[22] R. J. Gillespie and E. A. Robinson, Can. J. Chem. 41, 2074 (1963).
[23] D. W. J. Cruickshank, J. Chem. Soc. 5486 (1961).
[24] D. Barnard, J. M. Fabian and H. P. Koch, J. Chem. Soc. 2422 (1949).
[25] W. J. Lehmann, J. Mol. Spectrosc. 7, 261(1961).
[26] J. Brunvoll and I. Hargittai, Spectrosc. Lett. 10, 815 (1977).
[27] J. Kao, J. Am. Chem. Soc. 100, 4685 (1978).
[28] H. F. Hameka, J. Mol. Struct. 226, 241 (1991).
[29] J. Elguero, P. Goya, I. Rozas, J. Catalan and J. L. G. D. Paz, J. Mol. Struct. 184, 115 (1989).
[30] J. G. Angyan, C. Bonnelle, R. Daudel, A. Kucsman, and I. G. Csizmadia, J. Mol. Struct. 165, 273 (1988).
[31] T. Uno, K. Machida and K. Hanai, Spectrochim. Acta 27A, 107 (1971).
[32] K. Machida,Y. Kuroda and K. Hanai, Spectrochim. Acta 35A, 835 (1979).
[33] N. L. Allinger and Y. Fan, J. Comput. Chem. 14, 6655 (1993).
[34] M. Hotokka and R. Kimmelma, J. Mol. Struct. 276, 167 (1992).
[35] H. F. Hameka, S. L. Emery, G. R. Famini, J. O. Jensen, J. M. Leonard and D. J. Reutter, Phosphorus, Sulfur and Sillicon 53, 373 (1990).
[36] W. J. Hehre and W. A. Lathan, J. Chem. Phys. 56, 5255 (1972).
[37] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. D. Frees and J. A. Pople, J. Chem. Phys. 77, 3654 (1982).
[38] N. L. Allinger, M. Quinn, M. Rahman, and K. Chen, J. Phys. Org. Chem. 4, 647 (1991).
[39] C. -G. Zhan and Z. -M. Hu, Magn. Reson. Chem. 32, 465 (1994).
[40] Z. -M. Hu and C. -G. Zhan, Magn. Reson. Chem. 33, 249 (1995).
[41] J. Wan and C.-G. Zhan, Theor. Chim. Acta 92, 61 (1995).
[42] Z. -M. Hu and C. -G. Zhan, Int. J. Quantum Chem. 52, 109 (1994).
[43] C. -G. Zhan and Z. -M. Hu, Theor. Chim. Acta 84, 511 (1993).
[44] J. Wan and C. -G. Zhan, Spectrochim. Acta A 51, 1665, (1995).
[45] C. -G. Zhan and J. Wan, Chem. Phys. Lett. 279, 35 (1997).
[46] Z. B. Maksic, Z. Meic and K. Kovacevic, Z. Naturforsch. 28a, 797 (1973).
[47] J. Howell, A. Rossi, D. Wallace, K. Haraki and R. Hoffmann, Quantum Chemistry Program Exchange No. 344, Department of Chemistry, Indiana University, Bloomington, IN.
[48] M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. 99, 4899 (1977).
[49] M. J. S. Dewar, M. L. Mckee and H. S. Rzepa, J. Am. Chem. Soc. 100, 3607 (1978).
[50] M. J. S. Dewar and C. H. Reynolds, J. Comput. Chem. 7, 140 (1986).