Transferable Scaling Factors for Vibrational Force Fields of Halogenated Molecules Based on Energy-Consistent Pseudopotentials

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Within the framework of the scaled quantum mechanical procedure (SQM), transferable scaling factors (TSF) have been determined for a set of natural internal coordinates involving bromine and iodine atoms. Thereby, energy-consistent relativistic pseudopotentials adjusted to multiconfiguration Dirac−Hartree−Fock atomic reference data were used for simulating the Br^{7+} and I^{7+} cores, and a density-functional (DFT) treatment was applied to the valence-electron system. The TSFs were used to compute the vibrational spectra of dibromofuroxan and diiodofuroxan. Excellent agreement with available experimental data has been achieved.

1. Introduction

Computing vibrational spectra of molecules containing heavy elements is hampered by two aspects: (a) the large number of core electrons in the heavy elements and (b) the restriction to the harmonic approximation within the calculation of the force constants. For both aspects, pragmatical solutions have been introduced a long time ago,[1,2] which enable the calculation of IR and Raman spectra with an accuracy sufficient for many applications. The solution to the first problem is the introduction of effective core potentials (ECP), which not only significantly reduce the number of basis functions needed for a proper description of the atom but also may account for relativistic effects. The second problem can be circumvented by the application of scaling factors to the harmonic force constant matrix in internal coordinates, the so-called SQM approach.[2,3] Both approaches, that is, ECP and SQM, are based on (least-squares) fitting procedures to highly accurate quantum chemical calculations or experimental data and are thus characterized by the determination of coefficients, which effectively absorb the effects to be modeled. However, in contrast to the SQM approach, the ECP concept has the advantage of being independent of the basis set used and the theoretical level of the electronic structure calculation. Consequently, the SQM coefficients must be considered less general.

Here, we report about new large-core pseudopotentials (i.e., ECPs) and SQM scaling factors for molecules containing I and Br atoms. Section 2 summarizes the determination of the ECPs, section 3 presents the generation of new transferable SQM scaling factors, and section 4 shows an application of both approaches to the vibrational spectra of dibromo- and diiodofuroxan.

2. Large-Core Pseudopotentials for Br and I

For the present work, the Br^{7+} and I^{7+} cores were simulated by energy-consistent relativistic pseudopotentials of the new MCDHF variety[4−9] generated by adjustment to multiconfiguration Dirac−Hartree−Fock (MCDHF) atomic reference data. These pseudopotentials are of a basically two-component form

$$V^{PP} = -\frac{Q}{r} + \sum_{l,j} V_{lj}(r) P_{lj} \quad \text{with} \quad V_{lj}(r) = \sum_k B_{lj,k}\, e^{-\beta_{lj,k} r^2} \tag{1}$$

Here, Q is the core charge ($Q = 7$ for Br, I), and P_{lj} is the projector onto functions of angular-momentum quantum numbers l, j with respect to the core in question. The radial potentials for the different l, j combinations are expanded into linear combinations of a small number of Gaussian functions; their parameters ($B_{lj,k}$, $\beta_{lj,k}$) are adjusted in such a way that formally nonrelativistic two-component atomic valence-only calculations, including V^{PP}, as closely as possible reproduce the all-electron valence spectrum obtained in fully relativistic four-component MCDHF calculations. The reference set comprises the following nonrelativistic orbital configurations for the X = Br, I atoms/ions: X^-, ns^2np^6; X, ns^2np^5, ns^1np^6, $ns^2np^4(n+1)s^1$, $ns^2np^4(n+1)p^1$; X^+, ns^2np^4, ns^1np^5, $ns^2np^3(n+1)s^1$, $ns^2np^3(n+1)p^1$; X^{2+}, ns^2np^3, ns^1np^4; X^{6+}, nd, $(n+1)$d, $(n+2)$d, $(n+3)$d, 4f, 5f, 6f, 7f [$n = 4$, 5 for Br, I, respectively]. The sp part of V^{PP} was adjusted to all relativistic states originating from the ground-state configurations of X^-, X, X^+, and X^{2+} in MCDHF-average-level (AL) calculations, whereas only the average energy of the relativistic states (instead of individual energies) was invoked for the fit in the case of the higher-lying configurations; the df part, in turn, was adjusted to the relativistic state energies of X^{6+}. The accuracy of the fitted valence spectrum is better than 0.01 eV for configurational averages, and <0.2 eV for spin−orbit (SO) splittings. The resulting parameters of V^{PP} are listed in Table 1. For use in molecular calculations, (6s6p)/[4s4p] Gaussian-type (GTO) valence basis sets have been energy-optimized, in SCF calculations with the new pseudopotentials, to the ns^2np^5 atomic ground states; these sets, which have to be supplemented by diffuse and polarization functions as necessary, are available on the web.[10] Both pseudopotentials and basis sets have already been tested and applied, in one- and two-component calculations for the Pb and Bi monohalides.[7,9] In the present paper, the new V^{PP} for Br and I are applied, in SO-averaged form, in one-component valence-DFT calculations for a variety of Br and I compounds. The (6s6p)/[4s4p] basis sets

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TABLE 1: Parameters (in au) for the MCDHF-Adjusted Seven-Valence-Electron Energy-Consistent Pseudopotentials of Br and I

		Br		I	
l	*j*	*B*	*β*	*B*	*β*
s	1/2	61.542 272	4.886 044	83.107 547	3.380 230
		9.118 892	2.631 499	5.099 343	1.973 454
p	1/2	54.005 305	3.966 603	81.897 060	2.925 323
		4.957 031	3.178 315	2.334 965	1.903 188
p	3/2	53.859 363	4.504 167	83.411 770	3.073 557
		3.837 093	1.729 109	2.626 693	1.119 689
d	3/2	18.651 674	3.623 711	20.586 381	1.999 036
		3.940 793	1.487 064	5.443 334	0.998 982
d	5/2	18.331 386	3.613 902	20.813 494	1.967 767
		4.091 613	1.488 553	5.279 002	0.972 272
f	5/2	−8.470 155	2.764 513	−27.480 026	2.928 812
				−0.346 617	0.287 352
f	7/2	−8.445 280	2.756 653	−27.169 663	2.904 069
				−0.478 944	0.489 380

are supplemented by a single set of d polarization functions (exponents: 0.338 for Br, 0.279 for I).

3. Transferable SQM Scaling Factors for Br and I

The most common approach for correcting computed vibrational spectra obtained from harmonic force constants is an overall scaling of the fundamentals by a uniform factor. This procedure accounts for systematic errors arising from anharmonicities, basis set deficiencies, and missing electron correlation contributions of the underlying electronic structure calculation. Consequently, uniform scaling factors have been published for a large variety of quantum chemical methods and basis sets.[11−13] While easy to apply, the uniform scaling of vibrational spectra remains largely unsatisfactory because anharmonicities differ significantly with respect to the nature of the vibrational mode and thus maximun deviations of 50 cm^{-1} or more may be observed for certain vibrations.[14] In the more sophisticated SQM approach,[3] several scaling factors are introduced, each of them to be applied to the force constants belonging to a well-defined group of internal coordinates. As a result, the SQM factors do not depend on the computational level and the basis set only, but also on the definition of the internal coordinates. Because the internal coordinates can be grouped according to their different nature, specific characteristics (e.g., strong anharmonic corrections) of certain functional motifs can easily be absorbed in the corresponding scaling factors. Thus, the absolute mean deviation and the absolute maximum deviation of this approach are significantly lower than for the uniform scaling.[11,15] Moreover, a scaling of the force constants is superior to a scaling of frequencies because it leads also to an improvement of the normal modes and thus the intensities. The transferability of the SQM factors from one molecule to another can be guaranteed when the fitting procedure is based on a large pool of well-assigned vibrational modes.

Recently, SQM transferable scaling factors (TSF) have been published for the B3LYP density functional in combination with the 6-31G(d) basis set and two different sets of internal coordinates. The first set comprises the nonredundant natural internal coordinates of Pulay et al.,[11,16,17] while the second set is given by the highly redundant primitive internal coordinates.[15] It is found that the accuracy of the SQM-scaled vibrational spectra with respect to the experimental reference spectra is almost identical for both sets of internal coordinates.[15] In this study, we rely on the widely used natural internal coordinates and thus extend the set of TSFs provided in ref 11. Consequently, the same density functional and the same basis set have been used in this work. Although the 6-31G(d) basis must be considered small by current standards, we used this basis set for consistency reasons and to enable the application of these TSFs to large molecules, while anharmonicities of small molecules should be treated less empirically by perturbational approaches[18,19] or the variational SCF method.[20,21]

TABLE 2: Transferable Scaling Factors for Br- and I-Containing Modes

internal coordinate	Br	I
X−Hal bond	1.140	1.069
XY−Hal angle	1.047	0.982
dihedral angle of conjugated systems	0.949	0.897
dihedral angle of single-bonded systems	1.011	1.037

For the generation of the TSFs for Br- and I-containing vibrational modes, particular care has been taken for establishing a reliable training set of experimental vibrational spectra. Because most vibrations of bromine and iodine can be found in the spectral region below 600 cm^{-1}, there are not very many studies in which these particular modes have been securely assigned. Thus, the training set used comprises the following 36 molecules: methyl bromide,[22] bromoform,[22] bromoethylene,[23] 2,3-dibromopropene,[24] acetyl bromide,[25] 3-bromopropene,[26] 1-bromo-2-methylpropane,[27] bromobenzene,[28] all-*cis*-1,2-dimethyl-3-bromocyclopropane,[29] dibromomaleic anhydride,[30] *o*-bromotoluene,[31] propionyl bromide,[32] 2-bromofuran,[33] *p*-bromonitrobenzene,[34] bromocyclohexane,[35] *p*-bromotoluene,[36] *N*-bromosuccinimide,[37] 2,5-dibromofuran,[33] *p*-bromophenol,[38] bromocyclopentane,[39] 1-bromopropane,[40] methyl iodide,[41] iodoethylene,[42] *trans*-diiodoethylene,[43] *cis*-diiodoethylene,[43] *p*-iodonitrobenzene,[44] iodocyclopentane,[39] allyl iodide,[45] 2-iodofuran,[33] iodoethane,[46] *o*-diiodobenzene,[31] *p*-diiodobenzene,[36] *o*-iodotoluene,[38] *p*-iodotoluene,[36] *N*-iodosuccinimide,[37] and 2-iodopropane.[47,48] It was found to be necessary to introduce four new scaling factors for each halogen (Hal). These correspond to X−Hal stretchings, XY−Hal bendings and two kinds of torsions, where X and Y denote C, N, or O atoms. The TSFs of the torsions were split into those of conjugated systems (i.e., characterized by a double bond of the two central atoms) and the remaining ones. The scaling factors for X−Hal out-of-plane modes were found to be very close to the general out-of-plane TSF given in ref 11 and were thus not be considered explicitly. Table 2 shows the optimized TSFs for bromine and iodine. The final scaling factors essentially were found to be independent of the other TSFs, that is, they changed only very little upon variation of the TSFs for C, N, O, and H (i.e., ±0.002). Therefore, they can be used together with the TSFs reported in ref 11 or the reoptimized set as provided by Baker et al.[15] From 29 Br stretching vibrations, an absolute mean deviation with respect to the experimental data of 5.7 cm^{-1} has been obtained. Consequently, the absolute average percentage error is about 1.3% and thus slightly larger than for molecules without halogens (i.e., 0.9%).[15] We attribute this to the range of the spectral region (i.e., 200−700 cm^{-1}) and the associated experimental uncertainties. The corresponding values obtained from 21 I stretching vibrations are 3.8 cm^{-1} and 1.0%. After determing the new scaling factors for Br and I, we have tested their transferability on a set of seven molecules not included in the training set, namely, 2,3-dibromofuran,[49] α-bromoacrolein,[50] 3-bromo-2-methylpropene,[51] *o*-dibromobenzene,[31] 1-iodopropane,[40] 2,5-diiodofuran,[33] and *p*-iodophenol.[38] The maximum deviation of the Br stretching vibrations of the test set was found to be 9.9 cm^{-1}, and that for the I stretchings was found to be 8.4 cm^{-1}.

A key step within the SQM procedure is the determination of sets of internal coordinates for which the corresponding force constants will be scaled by the same TSF. For instance, in ref 11, torsions were divided into *conjugated torsions* and *single-bonded torsions*. Doubtless, this splitting is meaningful because the conjugating π-system of a molecule lends a rigidity to the corresponding torsional modes that distinctly distinguishes them from the torsions in saturated systems. However, on the basis of a pool of about 1850 frequencies, we found that the torsional TSFs are very sensitive with respect to their definition. Therefore, we used a more clear-cut definition: for dihedral angles with all four atoms contributing to a ring system, we determined a TSF of 0.961, and for all other torsions, we obtained a value of 0.855. The new grouping of the torsions was found to be more robust and leads to slightly improved absolute mean deviations. Moreover, identifying a particular torsion as belonging to one of the aforementioned groups is easier for the new definitions than for the original ones. Nevertheless, TSFs for torsions must be considered more error prone than those referring to other internal coordinates. Because Br and I are terminating structural motifs, all of their torsions would belong to the non-ring-system group. However, to yield an improved accuracy for the torsions of the halogens, we maintained the original splitting (i.e., conjugated vs single-bonded torsions) of the torsions involving the halogens at the cost of a larger number of TSFs. The two torsional TSFs of the halogens are only marginally affected by the different definitions of the torsions belonging to the other atoms.

While all TSFs involving C, N, O, and H atoms were found to be below 1.0, most of the new scaling factors differ from that scheme. This holds true in particular for the X−Hal TSFs. The same effect was found for the scaling factor for X−Cl stretchings as discussed recently.[17,52] Consequently, effects due to anharmonicity and electron correlation, which usually lead to an overestimation of the harmonic frequency, must be overcompensated for in this case by a shortcoming of the computational method. The most obvious explanation for this result is an overestimation of the X−Hal bond length, which in turn leads to an underestimation of the harmonic force constant and thus the vibrational frequency. For first row systems, Martin et al. found that the B3LYP functional leads to an overestimation of single bonds by about 0.002 Å.[53] For the G2 test set computed at the B3LYP/6-31G(d) level, other authors[54] report values of up to 0.013 Å. For a discussion of this topic, see ref 55. However, none of these values suffices to explain the magnitude of the computed TSFs. For analyzing this effect in detail, we focused primarily on the TSFs for the X−Br stretching mode. Because an overestimation of the bond lengths may arise from deficiencies of the exchange−correlation functional or the incompleteness of the basis set or both, we performed geometry optimizations of methyl bromide at the RHF and DFT levels with large basis sets. While the methyl group has been described by a standard aug-cc-pVTZ basis,[59] three polarizing d functions ($\zeta = 0.706, 0.264, 0.105$) and additional diffuse s ($\zeta = 0.044$) and p ($\zeta = 0.031$) functions were used for the Br atom.[60] In comparison to the experimental C−Br bond length of 1.934 Å, the computed values are 1.938 Å (RHF) and 1.956 Å (B3LYP). The B3LYP/6-31G(d) bond length is 1.967 Å. This shows that, the overestimation of the C−Br bond length at the B3LYP/6-31G(d) level originates mainly from deficiencies of the B3LYP functional and to a lesser extent from the small 6-31G(d) basis set. To see whether the large X−Br TSF is due to the observed overestimation of the X−Br bond lengths, we computed the vibrational spectra of all molecules given in Table 3 with C−Br bonds frozen to the experimental values while all other geometrical parameters were taken from the B3LYP/6-31G(d) calculations described above. Within the least-squares optimization of the TSF, we froze all TSFs but the X−Br stretching factor to the values provided in Table 2 or as given in ref 11. If the overestimation of the X−Br bonds is responsible for the TSF being larger than 1.0, one would anticipate a value below 1.0 in case of the frozen geometrical C−Br bonds. We obtained the new factor to be 0.984 thus supporting the assumption that the large X−Br TSF is mainly caused by an insufficient description of X−Br bond lengths by the B3LYP functional. Because the TSFs compensate for these systematic errors, they have comparably little impact on vibrational spectra computed within the SQM procedure.

TABLE 3: C−Br Bond Lengths [Å] in Dependence of Different Scaling Factors

molecule	r_{exptl}	r_{calcd}	$c_{\mathrm{av}}r_{\mathrm{calcd}}$	c	λ	ref
3-bromopropene	1.961	2.009	1.971	0.976	1.136	26
methyl bromide	1.934	1.967	1.929	0.983	1.095	74
vinyl bromide	1.884	1.911	1.874	0.986	1.079	75
acetyl bromide	1.977	2.021	1.983	0.978	1.123	76
2-bromofuran	1.848	1.873	1.837	0.987	1.075	77
propionyl bromide	1.979	2.026	1.987	0.977	1.129	78

Moreover, if the TSFs of the stretching modes originate mainly from an overestimation of the bond length, it should be possible to derive TSFs from geometrical parameters only. Early in 1961, on the basis of Badger's rule,[56,57] Herschbach and Laurie[58] established an empirical formula for estimating force constants of diatomic molecules, that is:

$$f_{\mathrm{exp}} = \frac{(a_{ij} - b_{ij})^3}{(r_{\mathrm{e}} - b_{ij})^3} \qquad (2)$$

Here, r_{e} denotes the equilibrium distance and a_{ij} and b_{ij} are parameters depending on the position of the atoms in the periodic system (i and j indicate the corresponding rows). Using $f_{\mathrm{exp}} = \lambda f_{\mathrm{calc}}$ and $r_{\mathrm{e}} = cr_{\mathrm{calc}}$, we can estimate the scaling factor λ for X−Hal stretchings solely from geometrical information.

$$\lambda = \frac{(r_{\mathrm{calc}} - b_{ij})^3}{(cr_{\mathrm{calc}} - b_{ij})^3} \qquad (3)$$

Because of the lack of experimental data, meaningful mean values for c (denoted c_{av}) and λ (i.e., λ_{av}) could be computed for X−Br bonds only. The value of c_{av} was computed to 0.981 and λ_{av} to 1.106. Table 3 displays a selection of C−Br bond lengths and the corresponding scaling factors c and λ. The scaling factor of 1.106 is slightly smaller than the corresponding TSF (1.140) and thus accounts for 76% of its correction to the force constants only. However, because of the comparably small basis of six geometrical parameters, it has a larger uncertainty, and hence, we still consider the agreement as good. Consequently, it can be concluded that on the basis of geometrical information only the empirical Herschbach−Laurie formula provides a good guess for bond stretching TSFs of terminating atoms. Because there are usually many more experimental data for geometrical data than for vibrational spectra, this approach may open the possibility to obtain frequency scaling factors for structural motifs for which no experimental spectra are available. This ansatz appears to be particularly useful for inorganic substances. However, systematic studies are necessary to prove this statement explicitly. On the basis of the X−Br scaling factor, c_{av}, an average overestimation of these bonds by about

TABLE 4: Experimental and Calculated Vibrational Frequencies [cm^{-1}] of *ortho*-Dibromobenzene

no.	ν_{exptl}	ν_{calcd}	dev	int[a]	assignment
			A_1		
1	3067	3097.3	30.3	4.9	C−H str.
2	3067	3081.1	14.1	10.9	C−H str.
3	1567	1567.4	0.4	3.6	ring def.
4	1449	1451.5	2.5	52.1	H bend.
5	1268	1272.4	4.4	0.2	ring def.
6	1159	1163.9	4.9	0.0	H bend.
7	1106	1100.7	−5.3	28.9	ring def.
8	1035	1025.1	−9.9	7.3	ring def.
9	640	650.8	10.8	10.5	ring def.
10	375	384.9	9.9	3.3	C−Br str.
11	129	129.1	0.1	0.1	Br bend.
			A_2		
1	975	975.9	0.9	0.0	H oop
2	854	859.7	5.7	0.0	H oop
3	695	677.7	−17.3	0.0	ring torsion
4	494	497.1	3.1	0.0	ring torsion Br oop
5		114.5	0.0	0.0	ring torsion
			B_1		
1	940	940.2	0.2	1.1	H oop
2	745	755.8	10.8	47.5	H oop
3	431	434.4	3.4	4.3	ring torsion
4	217	209.6	−7.4	1.4	Br oop
			B_2		
1	3067	3094.1	27.1	3.0	C−H str.
2	3067	3068.0	1.0	2.0	C−H str.
3	1567	1569.9	2.9	9.7	ring def.
4	1431	1427.9	−3.1	21.3	H bend.
5	1255	1252.3	−2.7	6.9	H bend.
6	1107	1118.8	11.8	3.2	ring def.
7	1012	1015.8	3.8	46.0	ring def.
8	700	714.8	14.8	19.6	ring def.
9	358	367.1	9.1	0.0	Br bend.
10	251	256.8	5.8	0.5	C−Br str. & ring def.

[a] Intensities are given in km/mol. [b] oop = out of plane; bend. = bending, str. = stretching.

2% has been found for B3LYP/6-31G(d) computed structures. This value is about twice as large as the absolute average deviation reported by Bauschlicher[54] for the G2 test set.

In the following, the reliability of the scaling factors shall be demonstrated on a molecule of the test set, *ortho*-dibromobenzene, for which all vibrations have been securely assigned from experiment. The experimentally observed fundamentals and the computed frequencies are listed in Table 4. The 30 fundamental modes of *ortho*-dibromobenzene can be classified among the symmetry species of C_{2v} as $\Gamma = 11A_1 + 5A_2 + 4B_1 + 10B_2$. The vibrations with a predominant contribution of the Br atoms are $10A_1$, $11A_1$, $4A_2$, $4B_1$, $9B_2$, and $10B_2$. For all of these six modes, the deviations from the experimental data of Green[31] are below 10 cm^{-1}. Note that *ortho*-dibromobenzene is the molecule of the test set that shows the maximum deviation from experimental data. Although this deviation corresponds to an error of about 2.5%, the agreement must still be considered excellent. This example supports the transferability of the TSF presented in this study.

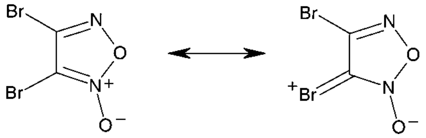
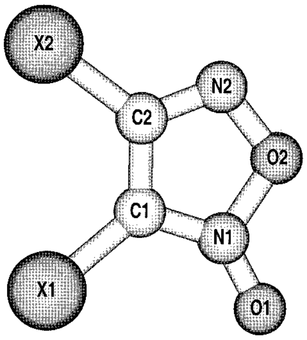


Figure 1. Mesomeric structures of dibromofuroxan.

TABLE 5: Geometrical Parameters [in Å and deg] of Dibromofuroxan (X = Br) and Diiodofuroxan (X = I)



bond	X = Br	X = I	angle	X = Br	X = I
C_1-C_2	1.422	1.427	$C_1-N_1-O_1$	135.5	135.5
C_1-N_1	1.355	1.337	$C_1-N_1-O_2$	105.6	106.0
C_2-N_2	1.303	1.306	$C_1-C_2-N_2$	112.1	111.9
N_1-O_2	1.464	1.461	$C_1-C_2-X_2$	126.4	127.2
N_2-O_2	1.372	1.371	$C_2-N_2-O_2$	106.6	106.9
N_1-O_1	1.215	1.216	$C_2-C_1-N_1$	107.0	106.7
C_1-X_1	1.854	2.039	$C_2-C_1-X_1$	131.3	131.9
C_2-X_2	1.869	2.059	$N_2-O_2-N_1$	108.7	108.5
			$O_1-N_1-O_2$	118.9	118.5
			$X_2-C_2-N_2$	121.5	120.9
			$X_1-C_1-N_1$	121.7	121.3

4. Vibrational Spectra of Dihalogenated Furoxans

The newly determined ECPs and SQM-TSFs were applied to the calculation of the vibrational spectra of dibromofuroxan and diiodofuroxan for which the low-lying vibrations involving Br or I are not known from experiment. For a recent review about the chemistry and generation of furoxans, see ref 61. The IR spectrum of dibromofuroxan has been measured by Pasinszki and Westwood.[62] The same authors computed the harmonic frequencies at the HF/6-31G(d) level. However, because of the low intensities of most vibrations, only about half of the vibrational frequencies have been assigned experimentally, and the computed fundamentals do not include electron-correlation effects. It has been shown recently that furoxans and benzofuroxans are extremely sensitive with respect to electron-correlation effects and thus the results depend strongly on the theoretical level applied.[63,64] For example, the endocyclic N−O bond of furoxan changes from 1.333 Å at the RHF/6-311G(2d,p) level to 1.511 Å at the MP2/6-311G(2d,p) level, while the experimental value is 1.441 Å.[65] Post-Hartree−Fock calculations including higher electron-correlation effects and the B3LYP hybrid functional were found to reproduce the geometrical parameters of furoxans with satisfactory accuracy.[66,67] Because a proper reproduction of geometrical parameters is an essential prerequisite for the calculation of vibrational spectra, the B3LYP exchange−correlation functional can be expected to yield force constants of the same quality as for standard molecules. Geometrical parameters of dibromofuroxan and diiodofuroxan obtained from B3LYP/6-31G(d) calculations making use of the new ECPs are provided in Table 5. As discussed in detail by Všetečka et al.,[68] dihalogenated furoxans can hardly be described by just one Lewis structure because the X_1 halogen serves as an electron donor. Consequently, at least the two mesomeric structures as shown in Figure 1 must be considered for a proper representation of the molecule. This, of course, is reflected in the geometrical parameters, as well as in the vibrational spectra. For both molecules, the C_2-X_2 and C_1-N_1 bonds are distinctly longer than the corresponding C_1-X_1 and C_2-N_2 bonds (cf. Table 5).

The computed frequencies of dibromofuroxan and diiodofuroxan are listed in Tables 6 and 7, respectively. The

TABLE 6: Calculated Vibrational Frequencies [cm^{-1}] of Dibromofuroxan

	expt		uniform scaling		TSF scaling		TSF(NO) scaling		
no.	ν	int[a]	ν	int[a]	ν	int[a]	ν	int[a]	assignment[b]
					A′				
1	1634	vs	1659.0	435.1	1660.8	432.8	1640.2	430.2	exocycl. NO str. and C═N str.
2			1454.7	2.2	1459.0	2.4	1458.3	1.6	C═N str.
3	1367	ms	1325.5	116.5	1351.6	120.8	1351.6	122.5	C−C str
4	1224	vw	1212.1	8.7	1228.9	16.2	1224.0	14.7	C═N str. and exocycl. NO str.
5	1014	m	1005.7	34.6	1026.1	31.1	1025.8	31.6	ring def. and endocycl. NO str.
6	969	ms	946.1	109.1	978.8	105.4	977.6	106.3	ring def. and endocycl. NO str.
7	803	m	783.8	34.8	802.3	30.6	801.0	32.5	ring def. and endocycl. NO str.
8	682	w	666.8	6.6	687.6	6.3	687.6	6.2	ring def. and exocycl. NO bend.
9	471	w	458.8	9.2	464.4	10.0	464.5	9.9	endocycl. NO str.
10			388.4	0.8	419.2	0.8	419.3	0.8	C−Br str.
11			314.6	0.7	338.9	1.6	338.8	1.6	C−Br str.
12			222.1	1.2	234.4	1.4	234.4	1.4	Br bend.
13			98.2	0.2	103.9	0.2	103.9	0.2	Br bend.
					A″				
1	641	vw	622.2	4.1	635.7	4.1	635.7	4.1	ring torsion and NO oop
2			548.5	0.7	560.4	0.6	560.4	0.6	ring torsion and NO oop
3			342.2	1.1	349.5	1.1	349.5	1.1	ring torsion and Br oop
4			224.0	1.3	229.7	1.2	229.7	1.2	Br oop
5			108.8	0.1	111.1	0.1	111.1	0.1	ring torsion and Br oop

[a] Intensities are given in km/mol [b] oop = out of plane; bend. = bending, str. = stretching.

TABLE 7: Calculated Vibrational Frequencies [cm^{-1}] of Diiodofuroxan

	uniform scaling		TSF scaling		TSF(NO) scaling		
no.	ν	int[a]	ν	int[a]	ν	int[a]	assignment[b]
				A′			
1	1645.8	460.6	1647.1	460.2	1626.0	459.7	exocycl. NO str. and C═N str.
2	1434.0	2.3	1434.9	3.0	1434.4	2.1	C═N str.
3	1288.3	84.7	1302.2	84.3	1302.2	85.2	C−C str.
4	1197.3	10.4	1208.5	16.9	1203.8	14.8	C═N str. and exocycl. NO str.
5	996.6	31.6	1011.1	26.4	1010.9	26.8	ring def. and endocycl. NO str.
6	927.5	98.8	954.2	98.1	953.3	98.3	ring def. and endocycl. NO str.
7	776.5	43.4	793.2	41.0	791.6	43.3	ring def. and endocycl. NO str.
8	655.7	8.0	671.3	8.1	671.2	7.9	ring def. and exocycl. NO bend.
9	458.2	7.9	462.8	8.8	462.8	8.8	endocycl. NO str.
10	332.8	1.5	350.4	1.7	350.4	1.7	C−I str.
11	266.4	1.7	281.4	2.3	281.3	2.3	C−I str.
12	192.1	1.7	199.4	1.7	199.4	1.7	I bend.
13	73.7	0.2	75.8	0.2	75.8	0.2	I bend.
				A″			
1	630.6	4.3	644.3	4.4	644.3	4.4	ring torsion and NO oop
2	555.6	0.7	567.4	0.6	567.4	0.6	ring torsion and NO oop
3	333.0	1.5	340.1	1.5	340.1	1.5	ring torsion and I oop
4	207.2	0.3	212.5	0.3	212.5	0.3	I oop
5	98.0	0.1	100.2	0.1	100.2	0.1	ring torsion and I oop

[a] Intensities are given in km/mol. [b] oop = out of plane; bend. = bending, str. = stretching.

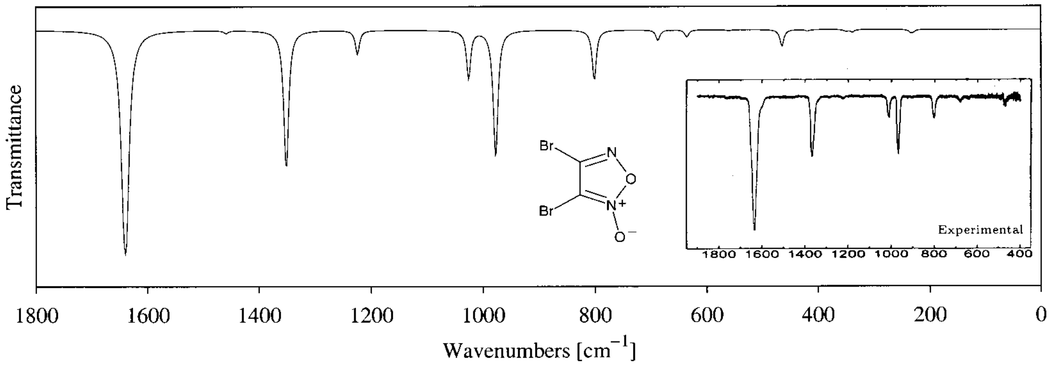


Figure 2. Simulated IR spectrum of dibromofuroxan. The experimental spectrum (inset) is reprinted with permission from Pasinszki, T.; Westwood, N. P. C. *J. Phys. Chem.* **1995**, *99*, 6401. Copyright 1995 American Chemical Society.

assignment of the fundamentals is based on the total energy distribution (M-matrix) technique as suggested by Pulay and Török.[69] Three different scaling procedures have been used for the investigation of these spectra: (1) a uniform scaling of all frequencies by a global factor of 0.963, (2) SQM scaling using the TSFs discussed above, and (3) SQM scaling with an extra scaling factor for the $\mathrm{N^+{-}O^-}$ stretching. A comparison of the uniformly scaled spectrum of dibromofuroxan with the experimental spectrum of Pasinszki and Westwood[62] yields a deviation of more than 40 cm^{-1} for the 3A′ mode. Moreover, within the uniform scaling approach, the C−Br stretchings (10A′ and 11A′) are scaled by a factor smaller than 1.0, while our SQM results indicate that a scaling factor significantly larger than 1.0 should be used. Consequently, *X−Br and X−I stretching modes computed at the B3LYP/6-31G(d) level cannot be corrected by global scaling schemes*. As a result, the vibrational spectra of dibromofuroxan and diiodofuroxan obtained from uniform scaling cannot be considered reliable. SQM scaling by the TSFs derived above and those provided in ref 11 results in a significantly improved overall agreement. With respect to the uniform scaling, the C−Br stretching fundamentals are corrected by up to 30 cm^{-1}. However, a maximum deviation of about 27 cm^{-1} for the 1A′ mode (i.e., a combined exocyclic $\mathrm{N^+{-}O^-}$ and endocyclic C═N stretching) indicates that *N*-oxidic stretchings should be scaled separately. This result is in agreement with previous studies in which a scaling factor of 0.880 has been suggested for exocyclic N−O bonds (including nitro groups).[70,71] On the basis of the experimental spectra of furoxan,[65] pyridine-*N*-oxide,[72] and pyrroline-*N*-oxide,[73] this factor has been reoptimized to 0.886 for the zwitterionic $\mathrm{N^+{-}O^-}$ moiety. Note that, for obtaining this factor, we did not rely on the experimental spectrum of dibromofuroxan. For molecules with other zwitterionic motifs, we anticipate similar deviations. The explicit consideration of the $\mathrm{N^+{-}O^-}$ bond leads to a particular improvement of the 1A′ and 4A′ modes. Within this approach, the maximum deviation has been reduced to 16 cm^{-1}. The absolute mean deviation is 6.9 cm^{-1}. In summary, the overall agreement with the recorded spectrum of Pasinszki and Westwood[62] is excellent, for a graphical comparison see Figure 2. Moreover, the computed vibrational spectrum of dibromofuroxan supports the arguments for the mesomeric structures of this molecule. The two C−Br stretching fundamentals differ by about 80 cm^{-1}, indicating a stronger bond for $\mathrm{C_1{-}Br_1}$ than for $\mathrm{C_2{-}Br_2}$. The spectrum of diiodofuroxan closely resembles that of dibromofuroxan (cf. table) and is thus not shown graphically. The largest difference between the two spectra can be observed for the 3A′ C−C stretching mode (∼49 cm^{-1}). Because of the steric hindrance of the bulky I atoms, this difference had to be anticipated.

5. Summary and Conclusions

A set of SQM-TSFs based on natural internal coordinates has been determined for Br- and I-containing organic molecules. These TSFs are tailored for the use with new MCDHF-adjusted seven-valence-electron energy-consistent pseudopotentials for Br and I, in connection with a B3LYP/6-31G(d) treatment of the valence shell. For calculations of this type, absolute mean deviations of 5.7 and 3.8 cm^{-1} were computed for Br and I stretching vibrations. Corresponding maximum deviations were found to be below 10 cm^{-1}. TSFs for these stretching modes are larger than 1.0, indicating too long C−Hal bonds. Consequently, these stretchings should not be scaled by factors below 1.0 as is usually done in the standard frequency scaling procedure. All fundamentals of dibromofuroxan and diiodofuroxan have been determined and assigned. Comparison with experimental data is excellent.

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