

Estimation of the ^{79}Br NQR Frequencies of Bromo-Containing Molecules Using *ab initio* Calculations at Different Levels

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Ab initio calculations of bromo-containing molecules on the RHF, B3LYP and MP2 levels and 6–31G(d), 6–31+G(d), 6–311G(d) and 6311+G(d) basis sets were executed. They were used to estimate the ^{79}Br NQR frequencies of these molecules. A satisfactory agreement between experimental and estimated NQR frequencies is obtained for the sum of populations of 13p- and 14p-components of the Br atom valence p-orbitals obtained from the RHF, B3LYP and MP2 calculations (particularly from RHF calculations) with the split valence basis sets 6–311G(d) and 6–311+G(d). The agreement between the experimental and estimated NQR frequencies is worse for the populations of the 9p-components of the Br atom valence p-orbitals obtained from these calculations with the basis sets 6–31G(d) and 6–31+G(d). An analogous conformity was not obtained using the populations of other components of the Br atom valence p-orbitals or their total populations obtained from all above-mentioned calculations.

Key words: *ab initio* Calculations; Valence p-orbital Populations; ^{79}Br NQR Frequency; Bromo-containing Molecules.

1. Introduction

Since the electric field gradient (EFG) at the nucleus of the indicator atom depends strongly on the distance between it and the charges which create this EFG (see, e. g., [1, 2]), we suppose that the NQR parameters which depend on this EFG are formed not by all the indicator atom valence p-shell, but by its less diffuse part (see, e. g., [3–5]). Therefore the numerous attempts to estimate the ^{35}Cl NQR frequencies (ν) and the asymmetry parameters (η) of the EFG at the ^{35}Cl nucleus for chloro-containing organic compounds using the populations of the Cl atom valence p-orbitals did not result in satisfactory accordance with experimental NQR parameters (see, e. g., [4]). At the same time such accordance is observed on using the populations of less diffuse 3p-components of the Cl atom valence p-orbitals obtained from *ab initio* calculations of organic and organometallic molecules at the RHF/6-31G(d) level (see, e. g., [3–5]). Recently it was shown [6] that agreement between experimental ^{35}Cl NQR frequencies and estimated ones, using the populations of less diffuse 3p-components of the Cl atom valence p-orbitals in chloro-containing organic molecules, is obtained as well from the calcu-

lations of these populations using the 6-31G(d) and 6-31G+(d) basis sets and other quantum-chemical methods: Becke's three-parameter hybrid method, where the non-local correlation is provided by Lee, Yang and Parr's gradient-corrected correlation functional (B3LYP) and the Hartree-Fock method, followed by a Møller-Plesset correlation energy correction, truncated at second order (MP2). The use of populations of other components of the Cl atom valence p-orbitals in these basis sets, or any components in the 6-311G(d) and 6-311G+(d) basis sets, do not bring agreement between experimental and estimated ^{35}Cl NQR frequencies [6]. Thus, only the populations of the less diffuse parts of the Cl atom valence p-orbitals, which correspond to 3p-components of these orbitals in the 6-31G(d) and 6-31G+(d) basis sets, adequately describe the Cl atom electron distribution in organic and organometallic molecules which determines the ^{35}Cl NQR parameters.

The agreement between experimental NQR parameters and estimated ones from *ab initio* calculations allows a thorough analysis of experimental NQR data, using the results of these calculations at the RHF/6-31G(d) and RHF/6-31G+(d) levels, and on the other hand allows to check the correctness of

quantum-chemical calculations of electron distributions in molecules using experimental NQR data (see, e. g., [4, 6–8]). The combined use of both methods allows to obtain more accurate information on peculiarities and mechanism of mutual atomic influence in organic and organometallic molecules. At present a great number of chloro-containing organic and organometallic compounds is studied using these two methods jointly (see, e. g., [4]). For the expansion of the possibilities of such a combined method for the study of organic and organometallic molecules, the conformity between experimental and estimated ⁷⁹Br NQR frequencies of some bromo-containing molecules was tested in this work.

2. Results and Discussion

We have performed *ab initio* calculations of some bromo-containing molecules at the RHF, B3LYP and MP2 levels and 6-31G(d), 6-31G+(d), 6-311G(d) and 6-311G+(d) split valence basis sets using the GAUSSIAN 94W Program [9]. These calculations were executed with total optimization of the molecular geometry. For the calculations molecules were selected as to their sizes, the presence of experimental ⁷⁹Br NQR spectra and the NQR frequency range of them. The experimental ⁷⁹Br NQR frequencies presented in [10] were used. In the calculations the origin of the coordinates was chosen to be the Br nucleus and the Z axis was in the Br–C (Br–B) bond direction. For the estimation of the ⁷⁹Br NQR frequencies of the molecules studied the total populations of the Br atom valence p-orbitals and their components as well the equation

$$\nu = (e^2 Q q_{\text{at}} / 2h) [-N_z + (N_x + N_y) / 2] (1 + \eta^2 / 3)^{1/2} \quad (1)$$

for the atoms with nuclear spin $I = 3/2$ [1] were used. The $e^2 Q q_{\text{at}} / 2h$ values (Table 1) in this equation were obtained from Br₂ molecule calculations using the corresponding method, basis set and experimental ⁷⁹Br NQR frequency for this compound at 77 K (382.520 MHz [10]).

In Tables 2–4 the ⁷⁹Br NQR frequencies of the molecules, calculated using the RHF (Table 2), B3LYP (Table 3) and MP2 (Table 4) methods and all above mentioned split valence basis sets are presented. In these Tables the NQR frequencies, estimated using the total populations of the Br atom valence p-orbitals and populations of their less diffuse 9p-components in the 6-31G(d) and 6-31+G(d) basis sets, and those estimated using the total populations and sum of popu-

Table 1. The $e^2 Q q_{\text{at}} / 2h$ values for the Br atom obtained from *ab initio* calculations of the Br₂ molecule at different levels, as well as the parameters of the correlation equation (2).

No.	Method	$e^2 Q q_{\text{at}} / 2h$	A	B	r
1	RHF/6-31G(d)	792.271	0.8410.079	16.03220.944	0.990
2	RHF/6-31+G(d)	785.269	0.8430.063	18.31816.618	0.994
3	B3LYP/6-31G(d)	629.870	0.8160.186	25.87349.022	0.946
4	B3LYP/6-31+G(d)	625.441	0.8270.151	25.95339.924	0.964
5	MP2/6-31G(d)	814.323	0.8270.090	21.35923.785	0.987
6	MP2/6-31+G(d)	805.373	0.8290.125	23.65732.899	0.975
7	RHF/6-311G(d)	629.810	0.9620.106	17.20727.845	0.987
8	RHF/6-311+G(d)	639.912	0.9720.091	15.50224.082	0.990
9	B3LYP/6-311G(d)	780.557	0.9280.156	22.66541.272	0.969
10	B3LYP/6-311+G(d)	773.064	0.9410.133	21.27335.109	0.978
11	MP2/6-311G(d)	625.084	0.9490.091	21.59923.934	0.990
12	MP2/6-311+G(d)	620.551	0.9650.108	18.11328.488	0.986

lations of two less diffuse 13p- and 14p-components in the 6-311G(d) and 6-311+G(d) basis sets are presented. The use of populations of 9p-components of the Br atom valence p-orbitals obtained from the calculations of corresponding molecules at the RHF/6-31G(d) and RHF/6-31G+(d) levels results usually in some understated values of the ⁷⁹Br NQR frequencies as compared to experimental ones, and the use of total populations in too high values. Evidently, 9p-components have insufficient sizes and do not fully reflect the Br atom electron distribution which determines the experimental ⁷⁹Br NQR parameters. However they describe this electron distribution to a significantly greater degree than the total populations. The use of the sum of populations of the 13p- and 14p-components of the Br atom valence p-orbitals, obtained from the calculations of corresponding molecules at the RHF/6-311G(d) and RHF/6-311+G(d) levels, results in satisfactory conformity with the experimental ⁷⁹Br NQR frequencies. The estimated NQR frequencies are evidently only higher for the BBBr₃ and BrCN molecules (Table 2). The satisfactory agreement between the estimated and experimental ⁷⁹Br NQR frequencies indicates that the sum of the populations of the 13p- and 14p-components of the Br atom valence p-orbitals describes adequately the electron distribution of these atoms in bromo-containing molecules which determines the experimental ⁷⁹Br NQR data. The ⁷⁹Br NQR frequencies estimated using the total populations of the Br atom valence p-orbitals obtained from *ab initio* calculations at the RHF/6-311G(d) and RHF/6-311+G(d) levels are always considerably higher than the experimental ones (Table 2).

Table 2. Experimental ⁷⁹Br NQR frequencies in MHz at 77 K (ν_e) [10] and those estimated using the total populations of the Br atom valence p-orbitals ($\nu(\Sigma p)$), the populations of their 9p-components (in the 6-31G(d) and 6-31+G(d) basis sets) and the sum of 13p- and 14p-components (in the 6-311G(d) and 6-311+G(d) basis sets). The calculations are executed by the RHF method.

Molecule	ν_e	RHF/6-31G(d)		RHF/6-31+G(d)		RHF/6-311G(d)		RHF/6-311+G(d)	
		$\nu(9p)$	$\nu(\Sigma p)$	$\nu(9p)$	$\nu(\Sigma p)$	$\nu(13p+14p)$	$\nu(\Sigma p)$	$\nu(13p+14p)$	$\nu(\Sigma p)$
BrCH ₃	264.508	239.536	307.183	237.457	297.733	263.292	321.523	263.655	322.105
BrC ₂ H ₅	248.745	228.765	297.706	226.546	286.483	253.193	312.204	252.219	309.980
BrCOCH ₃	215.221	203.117	269.185	208.298	258.112	226.092	281.597	229.831	281.130
BrCH ₂ COBr	292.500	266.868	327.691	266.935	310.258	299.631	343.226	298.879	339.154
	234.870	213.074	276.225	217.852	259.195	240.038	289.212	241.594	282.792
BrCN	354.637	314.419	359.027	314.987	332.290	370.590	391.662	368.829	379.389
BrCF ₃	301.984	258.882	320.195	274.734	314.387	297.393	338.261	312.714	347.301
BrC ₆ H ₅	268.856	238.014	309.569	241.302	282.621	272.814	324.438	270.089	317.259
C ₆ H ₅ COBr	229.685	207.025	269.892	213.587	248.538	234.766	285.089	237.735	276.504
BBr ₃	175.279	158.270	212.841	160.204	226.004	196.905	235.144	195.467	255.783
2-brompiridin	265.213	238.629	310.841	241.953	292.826	276.712	327.041	273.688	324.921
BrCH ₂ CH ₂ Br	260.790	234.995	300.765	234.601	285.065	261.947	315.919	261.401	311.352
CH≡CCH ₂ Br	274.690	256.094	318.264	256.088	303.915	286.902	334.545	286.064	328.170

Table 3. Experimental ⁷⁹Br NQR frequencies in MHz at 77 K (ν_e) [10] and those estimated using the total populations of the Br atom valence p-orbitals ($\nu(\Sigma p)$), the populations of their 9p-components (in the 6-31G(d) and 6-31+G(d) basis sets) and the sum of 13p- and 14p-components (in the 6-311G(d) and 6-311+G(d) basis sets). The calculations are executed by the B3LYP method.

Molecule	ν_e	B3LYP/6-31G(d)		B3LYP/6-31+G(d)		B3LYP/6-311G(d)		B3LYP/6-311+G(d)	
		$\nu(9p)$	$\nu(\Sigma p)$	$\nu(9p)$	$\nu(\Sigma p)$	$\nu(13p+14p)$	$\nu(\Sigma p)$	$\nu(13p+14p)$	$\nu(\Sigma p)$
BrCH ₃	264.508	256.813	321.034	253.757	318.841	277.912	328.170	277.677	328.673
BrC ₂ H ₅	248.745	244.453	309.166	241.280	304.712	266.404	317.458	265.366	314.449
BrCOCH ₃	215.221	200.474	255.823	206.396	251.700	215.927	263.834	221.759	262.557
BrCH ₂ COBr	292.500	276.096	329.742	275.519	319.451	303.191	339.253	303.232	334.088
	234.870	208.469	261.381	213.699	253.365	226.881	269.132	230.859	262.704
BrCN	354.637	298.181	328.962	299.188	309.752	343.665	358.840	342.673	346.022
BrCF ₃	301.984	262.021	312.164	282.783	317.212	292.933	327.381	312.927	338.148
BrC ₆ H ₅	268.856	239.912	297.466	243.278	270.475	268.524	312.161	267.334	302.825
C ₆ H ₅ COBr	229.685	202.434	250.947	209.162	238.086	219.840	262.130	225.250	253.271
BBr ₃	175.279	157.249	208.483	158.796	224.307	189.053	221.441	187.644	239.354
2-brompiridin	265.213	238.057	297.218	241.321	285.957	268.000	311.699	267.023	307.975
BrCH ₂ CH ₂ Br	260.790	249.210	308.502	247.339	300.881	272.117	317.256	271.797	311.978
CH≡CCH ₂ Br	274.690	267.462	324.088	266.863	314.013	291.631	332.595	291.615	326.153

The estimation of population of the Br atom valence p-orbitals and their components in the split valence basis sets 6-31G(d), 6-31G+(d), 6-311G(d) and 6-311G+(d), using the more precise quantum-chemical methods in which the electron correlation is taken into account (B3LYP and MP2), do not change much the results of estimating the ⁷⁹Br NQR frequencies. And what is more, the use of these methods for the estimation of populations of 9p-components or sum of 13p- and 14p-components of the Br atom valence p-orbitals in corresponding basis sets do not improve much the agreement between the experimental and estimated NQR frequencies (Table 3, 4). On using the populations of other components of the Br atom valence p-orbitals (or their combinations) in all above

mentioned methods and basis sets, the agreement between the calculated and experimental ⁷⁹Br NQR frequencies is bad, as it is in the case of the total populations (Tables 2–4).

The linear correlations

$$\nu_c = A\nu_e + B \quad (2)$$

between the experimental ⁷⁹Br NQR frequencies for bromo-containing compounds and estimated ones using the populations of 9p-components of the Br atom valence p-orbitals in the 6-31G(d) and 6-31G+(d) basis sets, or using the sum of populations of 13p- and 14p-components in the 6-311G(d) and 6-311G+(d) basis sets, are observed.

Table 4. Experimental ⁷⁹Br NQR frequencies in MHz at 77 K (ν_e) [10] and those estimated using the total populations of the Br atom valence p-orbitals ($\nu(\Sigma p)$), the populations of their 9p-components (in the 6-31G(d) and 6-31+G(d) basis sets) and the sum of 13p- and 14p-components (in the 6-311G(d) and 6-311+G(d) basis sets). The calculations are executed by the MP2 method.

Molecule	ν_e	MP2/6-31G(d)		MP2/6-31+G(d)		MP2/6-311G(d)		MP2/6-311+G(d)	
		$\nu(9p)$	$\nu(\Sigma p)$	$\nu(9p)$	$\nu(\Sigma p)$	$\nu(13p+14p)$	$\nu(\Sigma p)$	$\nu(13p+14p)$	$\nu(\Sigma p)$
BrCH ₃	264.508	237.289	307.109	235.182	297.675	262.679	322.716	262.990	323.222
BrC ₂ H ₅	248.745	226.092	297.348	223.806	286.120	252.786	313.808	251.730	311.413
BrCOCH ₃	215.221	210.780	271.337	216.120	261.365	231.358	285.230	235.740	285.040
BrCH ₂ COBr	292.500	266.891	328.571	266.975	311.400	299.341	344.159	298.721	339.941
	234.870	220.701	278.331	225.782	262.362	244.403	291.847	246.727	285.736
BrCN	354.637	312.527	359.966	312.967	333.643	367.749	390.915	365.902	377.695
BrCF ₃	301.984	268.793	327.674	285.183	322.846	305.082	344.857	320.471	353.867
BrC ₆ H ₅	268.856	236.576	309.469	239.636	282.749	272.223	325.409	269.517	317.999
C ₆ H ₅ COBr	229.685	215.100	272.207	221.869	264.827	240.815	289.438	238.420	282.847
BBr ₃	175.279	155.572	212.570	157.354	225.596	194.336	234.176	192.773	254.784
2-brompyridin	265.213	240.303	312.119	243.407	294.504	278.214	329.002	275.446	326.824
BrCH ₂ CH ₂ Br	260.790	232.506	300.200	232.031	284.493	260.600	316.588	259.844	311.906
CH≡CCH ₂ Br	274.690	254.360	317.530	254.474	303.817	286.182	335.177	285.540	329.104

The parameters of the correlation equations (2) are presented in Table 1. The free term is nearer to “0” and coefficient *A* is nearer to “1” in this equation the agreement between estimated and experimental NQR frequencies is better. According to these criterions the best agreement between them is observed at the estimation of NQR frequencies using the sum of populations of 13p- and 14p-components of the Br atom valence p-orbitals obtained from *ab initio* calculations of molecules at the RHF/6-311G(d) and, particularly, at the RHF/6-311+G(d) level (Table 1). At the same time the best correlation coefficient (*r*) is observed at the NQR frequency estimation using the populations of 9p-components of the Br atom valence p-orbitals obtained from calculations at the RHF/6-31+G(d) level. However the correlation coefficient do not show the extent of agreement between the correlated values.

Thus, the best agreement between estimated and experimental ⁷⁹Br NQR frequencies is observed when estimating the NQR frequencies using the sum of populations of 13p- and 14p-components of the Br atom valence p-orbitals obtained from *ab initio* calculations at the RHF/6-311G(d) and RHF/6-311+G(d) levels. The partial taking into account of electron correlation in

the B3LYP method or more full taking into account of it in the MP2 method does not improve this agreement. The estimation of the ⁷⁹Br NQR frequencies, using the populations of 9p-components of the Br atom valence p-orbitals obtained from *ab initio* calculations of molecules by the RHF, B3LYP and MP2 methods and 6-31G(d) and 6-31G+(d) basis sets, brings considerably worse conformity with experimental data, and estimation of these using the populations of other components of the Br atom valence p-orbitals or their total populations obtained from any of these methods and any of the four above mentioned basis sets, results in values which considerably differ from experimental ones. It is quite natural, that use of the ⁷⁹Br NQR spectra and *ab initio* calculations for the study of peculiarities and mechanisms of atomic interactions in molecules, only such results of quantum chemistry one may use which satisfactory describe that part of the Br atom electron distribution which determines the ⁷⁹Br NQR parameters. The agreement between experimental and estimated ⁷⁹Br NQR frequencies supports the conclusion [3–5] that the NQR parameters are not determined by the full indicator atom valence p-shell, but by its less diffuse part.

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