Ab Initio Calculation of ^{81}Br Nuclear Quadrupole Resonance Transition Frequencies for Brominated Aromatics (Flame Retardants)

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Brominated aromatics, used extensively as flame retardants, have been studied with ^{81}Br nuclear quadrupole resonance (NQR) spectroscopy. NQR requires lengthy frequency searches because ^{81}Br NQR transition frequencies in brominated aromatics are spread over a wide (40 MHz) range. We investigate the ability of ab initio calculations to narrow this search range by predicting ^{81}Br NQR transition frequencies for a series of brominated aromatics, using restricted Hartree−Fock (RHF) and Becke's three-parameter Lee−Yang−Parr density functional theory hybrid method (B3LYP). Basis sets used are of double and triple-ζ quality with varying degrees of polarization included on bromine. Geometries are the isolated molecules, with coordinates optimized for lowest energy. The results of calculations for nine simple brominated aromatics are fit against experimental frequencies and the fit is subsequently used to predict frequencies of larger, two-ring brominated aromatics (one is sold commercially as a flame retardant). Comparison to experiment shows the accuracy of this approach to be approximately 5 MHz, reflecting a significant, 8-fold decrease in the spectral range to be searched by experiment.

Introduction

The use of quantum chemical calculations to interpret nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), and gas-phase microwave spectra has a rich history.[1−11] Recent attention to NMR chemical shift calculations demonstrates a renewed interest for calculation of NMR properties.[12−14] Less attention has been focused on calculation of NQR transition frequencies, despite the widespread use of NQR spectroscopy in the study of materials containing ^{2}H,[15−17] ^{17}O,[17,18] ^{27}Al[1], ^{14}N,[17] ^{63}Cu/^{65}Cu,[19,20] ^{93}Nb,[21] ^{35}Cl,[20,22,23] ^{209}Bi,[20] ^{23}Na,[21] and ^{81}Br.[20,24] Of particular interest in this work are brominated aromatics, including flame retardants, recently studied by ^{81}Br NQR spectroscopy.[24] High-impact polystyrene (HIPS), used in manufacturing computer monitors, televisions, and business and electrical equipment, is made less flammable by the inclusion of up to 30% by mass brominated aromatics.[25] ^{81}Br NQR spectra are used to measure flame retardant dispersion in HIPS. The major obstacle for ^{81}Br NQR is the exceedingly wide spectral range—over 40 MHz for brominated aromatics! For instance, sweeps of only 3 MHz can take 6 h, even with an automatically tuned NQR probe. There is clearly a need for a predictive method for ^{81}Br NQR transition frequencies.

Prior to this work, the only existing predictive model for ^{81}Br transition frequencies was based on Hammett σ values.[24,26] These values relate the acidity of benzoic acid and substituted phenyl compounds to NQR transition frequencies, upon the premise that electronic effects of a substituent in one system are proportional to the electronic effects in another. While this model is useful for lightly meta- and para-substituted aromatics, it fails for heavily brominated flame retardants due to two issues related to ortho substituents: a lack of σ parameters for ortho substituents and steric effects not included in the Hammett model.[27]

In their solid-phase brominated aromatics are molecular crystals. While solid-phase calculations are possible by including the full-crystal structure, this limits one to systems with known structures. Few structures are available because heavily brominated aromatics as a class tend to be difficult to crystallize. In addition, computer memory requirements for solid-phase calculations are currently beyond our resources, due primarily to the large number of bromine atoms and the short hydrogen−bromine distances typically found in commercial flame retardants. The prediction of solid-phase NQR transition frequencies using gas-phase calculations is thus an area that needs exploration. Calculations of ^{81}Br NQR spectral parameters and transition frequencies via electric field gradient (EFG) calculations for small molecules now use larger, more complete basis sets and include electron correlation, scalar-relativistic corrections, and vibrational and spin−orbit coupling effects.[28−35] For small molecules, good correlations with experiment are being made using double-ζ basis sets including polarization.[36−39] Gas-phase microwave and solid-phase NQR frequencies typically differ by less than 10%[11] (for instance, the value of $e^2q_{zz}Q(^{81}\mathrm{Br})/h$ (MHz) for gas phase is 8.5% higher than solid phase for methyl halides[40] and 6.9% higher for bromobenzene[41]). In addition, intermolecular interactions in the solid phase lead to splittings of transition frequencies that would be expected in more symmetric, gas-phase molecules. These splittings are small compared to the differences between different types of brominated aromatics. Thus, there are two aspects that require investigation: (1) can gas-phase calculations reproduce experimental trends and narrow the frequency search range for experimental work and (2) can gas-phase calculations be used to predict the splittings of frequencies seen in the solid-phase. In this work, we investigate (1) and leave (2) for future work.

In this paper, we report the first ab initio calculations of ^{81}Br NQR transition frequencies of brominated aromatics. These calculations are the first on large Br-containing molecules and the first on a commercially available flame retardant. We present

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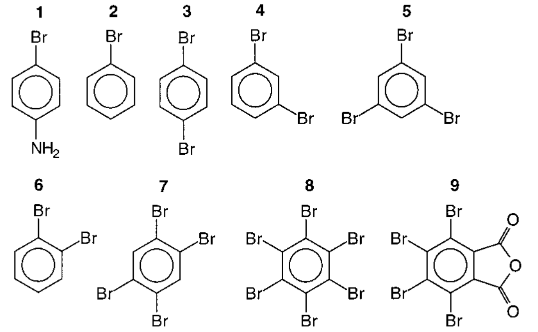

Figure 1. Simple brominated aromatics: (**1**) 4-bromoanaline; (**2**) bromobenzene; (**3**) 1,4-dibromobenzene; (**4**) 1,3-dibromobenzene; (**5**) 1,3,5-tribromobenzene; (**6**) 1,2-dibromobenzene; (**7**) 1,2,4,5-tetrabromobenzene; (**8**) hexabromobenzene; and (**9**) 3,4,5,6-tetrabromophthalic anhydride (flame retardant, tradename Saytex RB-49).

TABLE 1: Basis Sets

	Br			H, C, N, O		
level	notation[a]	ref[b]	source[b]	notation[a]	ref[b]	source[b]
double zeta	DZV	51	43	6-31G	52	43
	DZV(d)	51	43	6-31G	52	43
	DZV(df)	51	43	6-31G	52	43
triple zeta	TZV	53	54	TZV	55	43
	TZV(df)	53	54	TZV	55	43

[a] The polarization groups are explicitly shown in parentheses. [b] Ref refers to the original work for a basis set while source refers to where the explicit form was obtained.

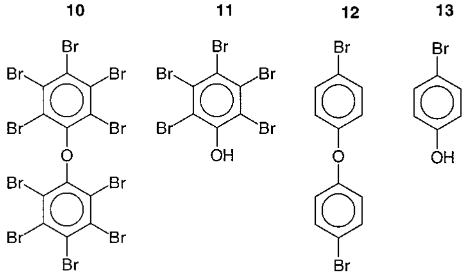

Figure 2. Flame retardant and models: (**10**) 1-(2,3,4,5,6-pentabromophenoxy)-2,3,4,5,6-pentabromobenzene (flame retardant, tradename Saytex 102); (**11**) truncated version of **10**; (**12**) 1-bromo-4-(4-bromophenoxy)benzene; (**13**) truncated version of **12**.

calculations of ^{81}Br NQR transition frequencies for a series of simple brominated aromatics and predict absolute frequencies of Br in larger brominated aromatics by fitting calculations to experiments.

Method

First, ^{81}Br NQR frequencies were calculated for the nine simple brominated aromatics shown in Figure 1. They were studied as isolated, gas-phase molecules. An initial geometry was generated using the SYBYL force field molecular mechanics routine in Spartan.[42] This was followed by a symmetry constrained, ab initio optimization in Cartesian coordinates using GAMESS[43] or Gaussian92.[44] The restricted Hartree−Fock (RHF) and Becke's three-parameter Lee−Yang−Parr density functional theory hybrid method (B3LYP) methods were applied using the five basis set combinations shown in Table 1. Previous calculations of EFGs for small molecules have correlated well with experiment. These calculations typically used a rather low level of theory (RHF) and relatively small basis sets (double-ζ + polarization). While trends among molecules can be reproduced, absolute errors are about 10%; in the case of brominated aromatics, this would lead to errors of 20−30 MHz, which is too large to be of practical value. The are no EFG calculations of large bromine-containing molecules, so it is unknown if small basis sets and RHF can accurately reproduce the experimental trends. In light of these observations, we decided to undertake a systematic study of basis sets and levels of theory, within the bounds of our computer resources. Hence, we investigated both double- and triple-ζ basis sets (with and without polarization) and RHF and B3LYP levels of theory. More accurate ways of including correlation, such as CI, were beyond the ability of our computer resources. The smaller basis sets are advantageous because calculations are faster, but are potentially less accurate than larger basis sets. RHF calculations do not include correlation, while B3LYP calculations approximately include correlation. For both the double- and triple-ζ basis sets, polarization functions were added to bromine's basis set while the other atoms' basis sets remained unchanged. Mixed basis sets were chosen because the majority of the EFG is local[45,46] and some basis sets are not available for Br. Sadlej's pVTZ [47,48] basis set, which is available for Br, was not used due to convergence difficulties for these molecules. Geometry optimization and ^{81}Br frequency calculation were performed using the same basis set and level of theory. EFG tensors were evaluated at Br in the optimized geometry. Then, EFG tensors were converted into the ^{81}Br $\nu(\pm{}^1/_2 \rightarrow \pm{}^3/_2)$ transition frequencies using the following relation:[24,11]

$$\nu(\pm{}^1/_2 \rightarrow \pm{}^3/_2) = (e^2 q_{zz} Q(^{81}\mathrm{Br})/2h)(1 + (\eta^2)/3)^{1/2}$$

$Q(^{81}\mathrm{Br})$, the quadrupole moment for the ^{81}Br nucleus, is 2.76 (4) × 10^{-29} m,[27,24] e is the charge of an electron, h is Plank's constant, q_{zz} is the largest component, and η is the asymmetry parameter of the diagonal EFG tensor. It is defined as $\eta = (|q_{yy}| - |q_{xx}|)/|q_{zz}|$. We follow the convention of ordering the eigenvalues of the traceless EFG tensor by absolute value such that $|q_{zz}| \geq |q_{yy}| \geq |q_{xx}|$. Conversion of q_{zz} from atomic units (and GAMESS sign convention) to MHz used the relation:

$$e^2 q_{zz} Q(^{81}\mathrm{Br})/h\ (\mathrm{MHz}) = q_{zz}\ (\text{atomic units}) \times (-64.85\ \mathrm{MHz/au})$$ [24]

The predictive ability of gas-phase calculations was investigated by using a linear fit of experimental, solid-phase frequencies to the calculated, gas-phase frequencies for the nine simple brominated aromatic molecules shown in Figure 1. The fits were used to predict the frequencies of 1-(2,3,4,5,6-pentabromophenoxy)-2,3,4,5,6-pentabromobenzene (Saytex 102) and 1-bromo-4-(4-bromophenoxy)benzene. These are molecules **10** and **12** in Figure 2, both recently studied. **10** is sold commercially as a flame retardant and **12** is used as a model for flame retardant dispersal.[24] CPU time considerations prevented calculations on **10** itself, forcing us to use a truncated version, **11**. For **12**, both the entire molecule and a truncated version (**13** in Figure 2) were studied. The comparison of the results of **12** and **13** was used to assess the relevance of the results from **11**.

Results and Discussion

The calculated and measured ^{81}Br NQR transition frequencies of all molecules are listed in Table 2 and Table 3. As necessary, the experimental frequencies are averaged over multiple lattice sites. For example, the average 231.228 MHz is reported for 1,3,5-tribromobenzene which has three crystallographically inequivalent bromine sites with observed transitions at 230.407,

TABLE 2: Experimentally Observed and Calculated ^{81}Br NQR Transition Frequencies (in MHz) for Simple Brominated Aromatics

			basis set (Table 1)									
			DZV		DZV(d)		DZV(df)		TZV		TZV(df)	
molecule (Figure 1)	expt	ref	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP
1	221.862	56	222.937	228.766	217.862	224.001	232.067	236.428	256.852	260.779	251.287	255.863
2	220.890	57	225.119	230.183	219.235	224.818	233.595	237.276	259.583	262.464	253.224	255.176
3	226.490	26	230.394	234.546	223.715	228.632	237.694	240.961	264.379	266.464	257.096	258.456
4	231.489a	58	231.638	235.400	224.776	229.385	238.683	241.605	265.583	267.370	258.271	259.275
5	231.228[a]	24	237.424	240.037	229.757	233.504	243.219	245.341	271.005	271.832	262.879	263.042
6	236.019[a]	59	239.863	244.639	232.418	236.465	246.178	247.930	275.381	277.718	266.562	265.878
7	239.701	24	247.945	248.502	239.573	241.201	252.685	253.202	283.083	281.866	272.954	270.917
8	255.196a	59	263.089	256.440	253.671	252.086	266.847	264.646	301.926	303.526	289.030	283.825
9′ [c]	253.080[b]	24	265.822	263.653	255.655	253.750	267.947	263.517	299.880	296.701	290.441	282.125
9″ [c]	254.293[b]	24	271.896	268.160	262.168	258.644	273.110	267.940	304.421	299.152	294.799	285.280

[a] Average of multiple transitions. [b] Average of two observed transitions assigned to this chemical site. [c] Here **9′** refers to crystallographic sites Br-3 and Br-6 and **9″** to Br-4 and Br-5.

TABLE 3: Experimentally Observed and Calculated ^{81}Br NQR Transition Frequencies (in MHz) for Flame Retardant and Models

			basis set (Table 1)									
			DZV			DZV(d)			TZV		TZVP	
molecule (Figure 2)	expt	ref	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP
12	228.117[a]	24	229.123	233.866	222.862	228.158	236.824	240.309	262.831	265.637	256.129	257.933
13		24	227.383	232.315	221.449	226.798	235.478	239.003	261.573	264.630	255.135	257.085
11	254.148[a]	24	260.756	258.120	251.946	250.557	264.442	262.346	297.724	293.228	285.722	280.677

[a] Average of multiple transitions.

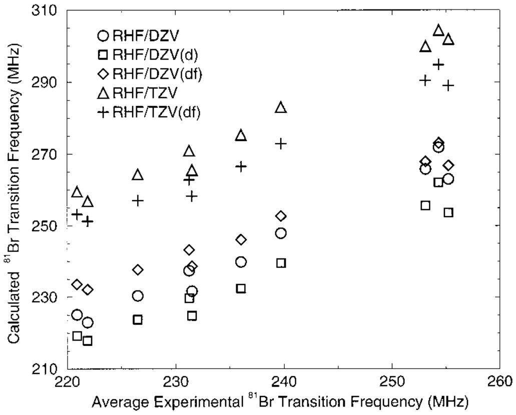

Figure 3. RHF calculated ^{81}Br NQR frequencies for simple brominated aromatics.

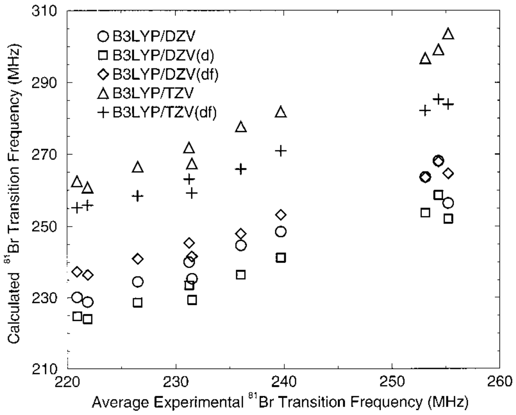

Figure 4. B3LYP calculated ^{81}Br NQR frequencies for simple brominated aromatics.

231.533, and 231.745 MHz.[24] Plots of experimental frequency versus calculated frequency for all basis sets are shown for RHF in Figure 3 and B3LYP in Figure 4. Differences in frequencies between unoptimized and ab initio optimized structures varied nonuniformly between 5 and 10 MHz. Thus, we deemed optimization important and report only the frequencies for the ab initio optimized structures. All basis sets and levels of theory adequately reproduce the experimental trends. Qualitatively, triple-ζ basis sets give frequencies about 10% higher than double-ζ basis sets and the polarization functions appear to affect frequencies only quantitatively. The gas-phase frequency for 1-bromobenzene is 240.034 MHz;[41] our calculations show that double-ζ basis sets underestimate this value by about 5−10% and the triple-ζ basis sets overestimate this value by 5−10%. This result, combined with the good reproduction of the trends among different brominated aromatics, suggests that both double and triple-ζ basis sets are adequate for brominated aromatics.

As a quantitative measure of the agreement between calculation and experiment, we calculated the rms errors and the maximum error made for each basis set and level of calculation. These are shown in Table 4. The double-ζ basis sets have rms errors around 10 MHz, while the triple-ζ basis sets have rms errors of about 30−40 MHz. The maximum errors have a similar pattern.

The trends among the brominated aromatics are well represented by gas-phase calculations, but absolute differences between calculation and experiment remain. We used a linear fit of experiment versus calculation to see if calculations, combined with a fit, could be used to accurately predict NQR transition frequencies. The values of our fitting parameters (slope and intercept) as well as the rms and maximum errors are given in Table 4. The fits give rms errors less than about 5 MHz. All basis sets, with the possible exception of DZ, give maximum errors on the order of 5 MHz using either RHF or B3LYP. The correlation coefficient shows the frequencies calculated with the larger basis sets to be very slightly more correlated with those from experiment.

We now turn to the predictive ability of the calculations. Using a linear fit, the ^{81}Br NQR transition frequencies were predicted for a flame retardant and a model for flame retardant

TABLE 4: Fitting Parameters, Rms Residuals, and Maximum Errors for Calculated and Fitted ^{81}Br NQR Transition Frequencies for Simple Brominated Aromatics

	basis set (see Table 1)									
	DZV		DZV(d)		DZV(df)		TZV		TZV(df)	
	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP
	Fitting Parameters									
correlation coeff	0.984	0.969	0.983	0.984	0.986	0.989	0.991	0.991	0.987	0.990
slope	1.326	1.022	1.202	0.944	1.136	0.887	1.365	1.198	1.225	0.892
intercept/MHz	−70.575	2.763	−49.040	14.438	−20.158	39.664	−45.335	−5.059	−20.616	56.574
	Rms residuals/MHz									
raw calculation	8.307	9.124	3.970	2.563	12.527	13.039	41.497	41.886	32.844	31.027
linear fit	2.271	3.377	2.366	2.268	2.106	1.836	1.643	1.727	2.026	1.747
	Max Error (Calculated − Experimental)/MHz									
raw calculation	17.603	13.868	7.876	4.352	18.817	16.386	50.129	48.330	40.507	34.286
linear fit	4.069	−7.011	4.599	4.332	3.769	−3.799	−3.714	−3.998	−3.760	−4.228

TABLE 5: Rms Residuals and Maximum Errors for Calculated and Predicted ^{81}Br NQR Transition Frequencies for Flame Retardant and Models

	basis set (Table 1)									
	DZV		DZV(d)		DZV(df)		TZV		TZV(df)	
	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP	RHF	B3LYP
	Rms Residuals/MHz									
raw calculation	3.882	4.706	5.064	2.209	8.869	10.557	37.520	37.719	28.934	28.472
linear fit	3.306	3.426	3.025	3.175	3.043	2.847	2.846	3.580	3.124	2.881
	Max Error (Calculated − Experimental)/MHz									
raw calculation	6.608	5.749	−6.668	−3.591	10.294	12.192	43.576	39.080	31.574	29.816
linear fit	−4.191	−4.319	−3.761	−4.088	−3.713	−3.361	−3.280	−5.064	−4.003	−3.311

dispersal, molecules **10** and **12** in Figure 2. Having two aromatic rings, both are significantly bigger than most of the simple brominated aromatics studied above and shown in Figure 1. **12** is small enough to perform a geometry optimization in a reasonable amount of CPU time, but **10** is too large to make such an exercise practical. As a result, truncated versions of **10** and **12** (**11** and **13**, respectively) were also studied. A comparison of the results from **12** and **13** was made to assess the impact of truncation. Since the EFG is a local property, it is not expected that there is a large inter-ring effect in either molecule (neither is a planar molecule[24]). Therefore, we truncated both molecules by the substitution of an −OH group for the duplicate ring. The frequencies for these three calculations are shown in Table 3. **13** proved to be a reasonable representation of **12**, differing in calculated transition frequencies by less than 2 MHz. As can be seen from the rms and maximum errors reported in Table 5, the agreement with experiment using the linear fit is quite good. For RHF and B3LYP with all basis sets agreement is within about 5 MHz.

Several comments can be made about the different basis sets and levels of theory. Neither the DZV or TZV basis sets give better than 5−10% absolute accuracy when compared to the gas-phase experimental result for 1-bromobenzene, indicating that larger basis sets are needed to obtain convergence on an absolute scale. However, both DZV and TZV, when used with a linear fit, accurately reproduce the experimental trend, indicating that both basis sets are adequate for estimating experimental frequencies. Overall, using a linear fit and RHF with the TZV basis set yields the most accurate results. The linear fit with RHF and the DZV basis set is nearly as accurate and can be used if computational resources are limited. Without the linear fit, using B3LYP with the DZV(d) basis set is also fairly accurate, this is probably due to a fortuitous cancellation of errors. When using a linear fit, polarization and correlation (using B3LYP) do not seem to improve the agreement between experiment and calculation. It is unclear whether this is due to the similarity between molecules studied here or to some more fundamental reason.

Conclusions

We calculated the EFG tensors at bromine sites in a series of simple brominated-aromatic compounds. RHF and B3LYP calculations using a double- or triple-ζ basis set and the linear fit prove capable of 5 MHz accuracy. The predictive capability of the calculations is demonstrated by comparing a prediction with known experimental frequencies for a commercial flame retardant and a model for flame retardant dispersal. Calculations are shown to be a useful tool for experimentalists looking for an NQR signal over a large range of frequencies. In the present case, the search range has been narrowed from 40 to 5 MHz, allowing a significant reduction in the time required to acquire data.

Three items prevent closer agreement of calculations and experiment: (1) differences between solid- and gas-phase systems, (2) deficiencies in the description of the electronic system such as omission of vibrational, spin−orbit, and scalar-relativistic effects, and (3) the value of the quadrupole moment for ^{81}Br.[49] Including the intermolecular effects that are present in the solid brominated aromatics is important, as is demonstrated by the splitting of transition frequencies seen in the solids. A simple method of including such effects, developed in a previous paper,[24] was not successful with the molecules studied in this work. Future work will investigate more systematic methods of including intermolecular interactions, such as representing other molecules in the crystal with point charges. Calculations that include scalar relativistic and spin−orbit effects were recently performed for HBr.[28] Frequencies calculated from that work (using the literature value of the Br quadrupole moment[7]) still differ with those from gas-phase experimental frequencies[50] by as much as 11%. The errors introduced through items 2 and 3 remain unresolved for small diatomic molecules and more exact methods remain computationally intractable for the large molecules we studied. However, the agreement seen here between predicted and observed frequencies demonstrates that calculations combined with fits can provide an effective procedure predicting experimental NQR frequencies.

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