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Parity-violation effect on vibrational spectra

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Weak nuclear coupling between the nucleons of a molecule and its electrons causes the energy and electronic wave function to be different for two enantiomers of a chiral molecule, i.e., for two molecules which are the specular image of each other. Although this effect has been known for some time, its magnitude is so small that all attempts made so far at measuring it experimentally have failed. We report in this paper computational estimates of vibrational frequency shifts due to parity-violation energy near or above current experimental resolution. Our findings indicate that an experimental evidence of parity-violation effects in molecular systems is within reach.

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INTRODUCTION

It has long been known that weak nuclear coupling between atomic nucleons and electrons in molecular systems is responsible for molecular parity-violation energy (E_{pv}), i.e., that the energy of an enantiomer, or chiral molecule, is different, in principle, from that of its specular image [1,2]. In practice, E_{pv} is so small that no direct experimental evidence has been found so far. Only indirect evidence was reported by Szabó-Nagy and Keszthelyi [3]. They detected a net enrichment of one enantiomeric form with respect to the other upon crystallization of chiral compounds of Co or Ir from a solution containing equal amounts of both forms. While providing an important proof that weak nuclear forces can influence chemical phenomena, their experiment does not provide a reliable quantitative measure of E_{pv} due to a number of assumptions on the kinetics of the crystallization process. To verify our understanding of parity violation in molecules, it is thus important to obtain more direct measurements of its effects. In this respect, theoretical estimates may prove extremely helpful in designing experiments likely to succeed.

E_{pv} originates from the exchange of virtual Z^0 bosons between an electron and a quark in the nucleus or between two electrons. Under ordinary conditions, the leading contribution to E_{pv} is due to the timelike component of the polar vector coupling to the nucleus and axial vector coupling to the electron. This gives rise to the effective parity-violation Hamiltonian [4,5]

$$H_{pv}=\frac{G_F}{\sqrt{8}}\sum_{N,i} Q_{W,N}\gamma_i^5\rho_N(\mathbf{r}_i), \tag{1}$$

where G_F is the Fermi coupling constant ($G_F=2.222\,55\times10^{-14}$ a.u.), the sum runs over all nuclei N and electrons i, $Q_{W,N}$ is the weak nuclear charge of nucleus N [$Q_{W,N}=-N_N+Z_N(1-4\sin^2\theta_W)$, where N_N and Z_N are the numbers of neutrons and protons in nucleus N, respectively, and θ_W is Weinberg mixing angle, assumed such that $\sin^2\theta_W=0.2315$], and $\rho_N(\mathbf{r})$ is the normalized nucleon density. The term γ_i^5 is Dirac's fifth matrix.

H_{pv} is the nuclear-spin free operator. Although there are additional parity-odd terms, their contribution to E_{pv} is small and they are usually neglected in molecular computations when nuclear-spin properties are not being addressed [5,6].

The first-order perturbative energy shift due to parity violation is the expectation value of H_{pv} with respect to a four-component relativistic wave function Ψ,

$$E_{pv}=\langle\Psi|H_{pv}|\Psi\rangle. \tag{2}$$

Within the Born-Oppenheimer approximation, the nuclei of a molecule move on the effective potential-energy surface (PES) determined by the electronic energy and wave function. In particular, the PES determines the vibrational motion near equilibrium geometries, including the molecular vibrational modes and frequencies. These are usually described up to third-order corrections within the harmonic approximation, i.e., by assuming that the PES is quadratic near the equilibrium geometry and, hence, that a normal-mode analysis of molecular vibrations is meaningful. Anharmonic corrections are usually treated as small perturbations to the harmonic potential.

Since E_{pv} reverses its sign in going from one enantiomer to its specular image, it has opposite effects on the corresponding PES. In particular, the PES curvature and anharmonic correction along a normal mode have opposite sign for the two enantiomers, resulting in opposite frequency shifts. The observable frequency difference between two enantiomers $\Delta\nu$ is thus twice the frequency shift computed for one of the chiral forms.

Due to the nature of the parity-violation interaction and due to our qualitative understanding of it [7], we expect E_{pv} to be larger for systems containing at least two heavy atoms close to each other in a highly asymmetric environment. Since E_{pv} vanishes for symmetric configurations, we expect the PES curvature and anharmonic correction to be proportional to E_{pv} for vibrations leading to symmetric configurations. One example of such a vibrational mode is a bending mode about a single chiral center leading to configuration inversion. In view of these considerations (see Ref. [7] for a

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more detailed discussion on this topic), we expect the H-Bi-*X* bending mode ($X=\mathrm{Br}$, I) in the molecules BiHFBr and BiHFI to exhibit E_{pv} corrections to the PES close to the maximal possible values for single chiral centers that do not involve radioactive elements. With the investigation of these systems, we provide a plausible, although not rigorous, upper bound on the effects of parity violation on small molecules.

EXPERIMENTAL RESOLUTION

Several estimated frequency shifts have been published for small organic molecules [8–12]. Unfortunately, these are orders of magnitude below current spectroscopic resolution, which under optimal conditions is as high as a few hertz [13–15]. At the same time, a serious attempt is being made at achieving enough spectroscopic accuracy to observe the predicted frequency shift for the C-F stretching mode of the molecules CHFClBr or CHFBrI [12,13,15]. Although this molecule proved convenient both for computational estimates and experimental sample preparation, the predicted frequency shift is still orders of magnitude beyond experimental reach.

In this paper, we report shift estimates for selected compounds, which match the reported experimental resolution. Although the molecules we studied may be less convenient to handle than CHFClBr, they are expected to have considerably larger shifts and may thus provide an alternative path to verify experimentally our understanding of molecular E_{pv}.

COMPUTATIONAL DETAILS

Optimal geometry and Hessian for BiHFBr and BiHFI were computed using nonrelativistic *ab initio* techniques, namely, second order Møller-Plesset perturbation theory (MP2) as implemented in the commercial program GAUSSIAN98 [16]. The basis set chosen is of double-ζ plus polarization quality on the light atoms and double-ζ with relativistic effective core potential (ECP) on the heavy atoms [17].

Geometries, normal modes, and vibrational frequencies were then used to estimate E_{pv} corrections to the PES near the minimum and the corresponding shifts in vibrational spectra. The corrections were obtained by computing E_{pv} at equilibrium geometry and at six geometries displaced by ± 0.02, ± 0.04, and ± 0.06 mass weighted atomic units along a selected normal mode corresponding by and large to the H-Bi-*X* angle bending ($X=\mathrm{Br}$, I). A parabolic least-square fit to the computed values was used to extract the force constant corrections. E_{pv} was computed at the Dirac-Coulomb-Hartree-Fock level using the program DIRAC [18]. The large component basis set was obtained from the uncontracted double-ζ basis sets by Dunning [19] and Dyall [20] adding tight *p* exponents and is described in detail in Ref. [7]. The small component basis set was obtained by strict kinetic balance as implemented in DIRAC. A Gaussian distribution was assumed for nuclear charge and nucleon density with the default exponents provided by DIRAC.

TABLE I. Computed parity-violation energies for the *R* enantiomer E_{pv} (10^{-14} a.u.), vibrational frequencies ω (cm^{-1}), and frequency shifts $\Delta\nu$ (Hz). Spectroscopic parameters were obtained within the harmonic approximation.

Level	BiHFBr			BiHFI		
	E_{pv}	ω	$\Delta\nu$	E_{pv}	ω	$\Delta\nu$
MP2 [a]	0.9	567	9.3	2.9	550	23.7
HF [a]	0.9	602	8.6	2.4	581	21.9
DFT [a]	1.0	540	10.1	3.5	520	26.6
MP2 [b]	1.2	575	11.7	3.4	556	26.9

[a] Basis set and ECP as in Ref. [17].

[b] Basis set as in Ref. [17] but with an alternative ECP [25].

RESULTS AND DISCUSSION

Within the harmonic approximation, the computed frequency shifts $\Delta\nu$ are 9.3 and 23.7 Hz for BiHFBr and BiHFI, respectively. For both molecules, the *R* enantiomer is predicted to have higher frequency than the *S* enantiomer.

Our estimates of $\Delta\nu$ depend mainly on three approximations: (a) the computational method used to calculate E_{pv} and its geometrical dependence, (b) the geometry and Hessian used, and (c) the harmonic approximation for the vibrational motion of the nuclei.

The computational method is approximate for a number of reasons. Based on previous investigations [4,5], we estimate the error on E_{pv} associated with the use of an approximate parity-violation Hamiltonian and Gaussian nuclear charge distribution to be of the order of a few percent. The lack of electronic correlation is expected to result in errors of the order of 10% [21], while the error due to the neglect of two-electron integrals involving only small components should be a fraction of a percent [5,21]. The fact that the basis set used in not complete, should contribute another few percent [21] to the error. In summary, the overall error bar associated with our values for E_{pv} is $\approx 15–20\,\%$. This error is systematic and we expect it to apply also to the geometrical dependence of E_{pv}, i.e., on the linear and quadratic fitting coefficients used to estimate the frequency shift.

Equilibrium geometries and Hessians were computed at the MP2 level using an ECP [22,23] on the heavy atoms. The dependence of our results on the computational level was tested by repeating the frequency shift computation with geometries and Hessians obtained at the Hartree-Fock and density-functional theory (DFT) [24] levels. The shifts obtained are all within about 10% of the MP2 result and 20% of each other (see Table I). To test the frequency shift dependence on the ECP used, we repeated the computation using geometries and Hessians obtained at the MP2 level with an alternative ECP [25]. As reported in Table I, the estimated frequency shift increases by $\approx 15–25\,\%$. From these results, we estimate the uncertainty due to the use of approximate geometries and Hessians to be of the order of 25–45 %.

The limits and advantages of the harmonic approximation are well known in the scientific community and will not be discussed here. The normal-mode description provided by

TABLE II. Computed parity-violation energies for the *R* enantiomer E_{pv} (10^{-14} a.u.), vibrational frequencies ω (cm^{-1}), infrared transition intensity *I* (km/mol), and frequency shifts $\Delta\nu$ (Hz). Spectroscopic parameters include anharmonic corrections as described in the text.

Level	BiHFBr			BiHFI		
	ω	I	$\Delta\nu$	ω	I	$\Delta\nu$
			Fundamental transition			
MP2 [a]	447	27.23	7.5	506	28.05	17.8
HF [a]	520	29.55	4.8	494	30.40	14.1
DFT [a]	296	20.14	18.9	452	20.64	23.8
MP2 [b]	486	22.80	8.3	379	26.36	27.4
			First overtone			
MP2 [a]	776	0.03	15.0	1011	0.09	35.6
HF [a]	962	0.16	9.6	899	0.10	28.2
DFT [a]	440	0.26	37.8	877	0.02	47.6
MP2 [b]	882	0.10	16.5	566	0.00	54.8

[a] Basis set and ECP as in Ref. [17].

[b] Basis set as in Ref. [17] but with an alternative ECP [25].

the harmonic approximation is expected to be correct within the error bar already present in our results, at least for the vibrational modes we are investigating. The effect of anharmonicity on the frequency and the frequency shift, on the other hand, is not negligible. We computed the total energy at 49 points along the normal-mode coordinate in the region where the potential is lower than the vibrational zero-point energy. The fourth degree fit to these points contains small but significant third and fourth degree coefficients. Including the perturbative effect of these terms on the frequency, we obtain the values reported in Table II. Due to the presence of third-order terms, the infrared intensity for the first overtone does not vanish and we include in Table II also the computed spectroscopic parameters for this transition. We observe that the anharmonic treatment depends strongly on the computational method used to compute the normal coordinate. For instance, some of the methods predict the first overtone to fall in the CO_2 laser operating range ($850-1120\ \mathrm{cm}^{-1}$), while other methods compute the corresponding frequency to be too low. All methods indicate that the intensity of the first overtone should be a small fraction of the fundamental intensity and thus that the transition should be harder to investigate experimentally. Due to the wide range of predicted results, we cannot estimate if the four orders of magnitude gain in the frequency shift with respect to other transitions in the CO_2 laser range could compensate for this.

In conclusion, we estimate the reported frequency shifts to be correct up to about 40–60%. In particular, we expect the predicted order of magnitude to be significant.

STABILITY OF MOLECULES

We are not aware of molecular BiHFBr or BiHFI ever having been synthesized or isolated. It is thus relevant to assess whether or not they would be stable under the conditions required to perform high-accuracy spectroscopic measurements. A very approximate estimate is obtained as follows.

The vapor pressure is known for $BiCl_3$ [26] and $BiBr_3$ [27] and is well interpolated by a three-parameter fitting equation (see Refs. [26] and [27] for details) for temperature ranges of 503.6–710.5 K and 534–734 K for $BiCl_3$ and $BiBr_3$, respectively. By extrapolating outside the fitting ranges we can provide a crude guess for the vapor pressure at lower temperatures, i.e., for the boiling temperatures at lower pressures, for these two species. Assuming this temperature changes linearly with the molecular weight, we guess that BiHFBr and BiHFI will produce a vapor pressure of 1×10^{-6} bars at about 334 and 352 K, respectively. Based on these, we guess that a plausible working temperature could be as low as 340 K. We stress the fact that these values are not reliable estimates, which we are not able to produce, but only our best guess based on available experimental data on similar compounds. Although we use 340 K to complement our discussion with explicit numbers, in the absence of experimental measurements this value is not to be taken as a lower bound to the working temperature.

We obtain a crude estimate of whether or not BiHFBr and BiHFI would be stable at 340 K as follows. Geometries, energies, and vibrational frequencies were computed at the (nonrelativistic) MP2 level [17] for the isolated molecules and all possible diatomic decomposition products. For each of these species, the Gibbs free energy *G* was obtained by applying standard statistical-mechanics techniques [28]. To this end, we assumed all species to behave as ideal gases and the harmonic approximation to hold for all vibrational modes. Also, although at the nonrelativistic MP2 level the ground state for diatomic molecules containing Bi has triplet spin multiplicity, we neglected the electronic contribution to the entropy, because at the more correct relativistic level the ground state is singlet. The results show that the only spontaneous decomposition reaction is $\mathrm{BiHF}X\rightarrow\mathrm{Bi}X+\mathrm{HF}$ ($\Delta G=-38$ and -45 kJ/mol for $X=$Br and I, respectively). For this reaction we located the transition state and computed the corresponding activation free energy of 195 (Br) and 190 (I) kJ/mol. This suggests that the dissociation reaction should be slow at the conditions considered, provided neither the reactants nor the products catalyze the reaction. Other decomposition pathways, e.g., to form metallic bismuth, are likely to start via one of the decomposition reactions we considered. Hence, even though, for instance, we expect the reaction $\mathrm{BiHFBr}\rightarrow\mathrm{Bi}_{(s)}+\mathrm{HF}_{(g)}+\frac{1}{2}\mathrm{Br}_{2(g)}$ to be exothermic by about 140 kJ/mol, it would have the same activation barrier of 195 kJ/mol. Similar results are obtained at the DFT level.

We also investigated the configuration inversion reaction, i.e., the reaction transforming one enantiomer into its specular image. The transition state for this process is planar and we compute the activation free energy at 138 and 139 kJ/mol for BiHFBr and BiHFI, respectively. This indicates that a significant enantiomeric enrichment could be maintained for the time scale of several hours required to perform the measurement.

In short, the molecules we suggest do not satisfy current requirements for spectroscopic observation of the frequency shift [12,15] for two main reasons: (a) they do not exist and

(b) they do not have a fundamental transition in the CO_2 laser operating range. According to our reasoned guess, however there is no fundamental reason why the molecules could not be synthesized. Also, even if its intensity is expected to be small, it is possible for the first overtone transition to lie in the CO_2 laser range.

CONCLUSIONS

We investigated with *ab initio* computational techniques the effect of parity violation due to weak nuclear forces on selected vibrational frequencies in two chiral molecules, namely, BiHFBr and BiHFI. We estimate the magnitude of the resulting frequency shift to be at least comparable to current experimental resolution as reported for investigations on other systems. We briefly discuss the stability of the selected molecules and indicate possible problems that may arise while preparing and handling the samples in view of a spectroscopic measure.

Despite the prohibitive technical problems associated with a measurement on the molecules we studied, our results indicate that parity-violation effects in molecular systems can be at or above current detection limits. Hence, the search for parity-violation effects in molecules does not necessarily require further spectroscopic enhancements and progress in chemical synthesis could lead to the desired results as well.

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