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Silver Nyambo

Marquette University

Cyrus Karshenas

Marquette University

Scott Reid

Marquette University, scott.reid@marquette.edu

Phalgun Lolur

Missouri University of Science and Technology

Richard Dawes

Missouri University of Science and Technology

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Citation: *The Journal of Chemical Physics* **142**, 214304 (2015); doi: 10.1063/1.4921466

View online: <http://dx.doi.org/10.1063/1.4921466>

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Towards a global model of spin-orbit coupling in the halocarbenes

Silver Nyambo,¹ Cyrus Karshenas,¹ Scott A. Reid,^{1,a)} Phalgun Lolur,² and Richard Dawes^{2,a)}

¹Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233, USA

²Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409, USA

(Received 9 March 2015; accepted 11 May 2015; published online 3 June 2015)

We report a global analysis of spin-orbit coupling in the mono-halocarbenes, CH(D)X, where X = Cl, Br, and I. These are model systems for examining carbene singlet-triplet energy gaps and spin-orbit coupling. Over the past decade, rich data sets collected using single vibronic level emission spectroscopy and stimulated emission pumping spectroscopy have yielded much information on the ground vibrational level structure and clearly demonstrated the presence of perturbations involving the low-lying triplet state. To model these interactions globally, we compare two approaches. First, we employ a diabatic treatment of the spin-orbit coupling, where the coupling matrix elements are written in terms of a purely electronic spin-orbit matrix element which is independent of nuclear coordinates, and an integral representing the overlap of the singlet and triplet vibrational wavefunctions. In this way, the structures, harmonic frequencies, and normal mode displacements from *ab initio* calculations were used to calculate the vibrational overlaps of the singlet and triplet state levels, including the full effects of Duschinsky mixing. These calculations have allowed many new assignments to be made, particularly for CHI, and provided spin-orbit coupling parameters and values for the singlet-triplet gaps. In a second approach, we have computed and fit full geometry dependent spin-orbit coupling surfaces and used them to compute matrix elements without the product form approximation. Those matrix elements were used in similar fits varying the anharmonic constants and singlet-triplet gap to reproduce the experimental levels. The derived spin-orbit parameters for carbenes CHX (X = Cl, Br, and I) show an excellent linear correlation with the atomic spin-orbit constant of the corresponding halogen, indicating that the spin-orbit coupling in the carbenes is consistently around 14% of the atomic value. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921466>]

I. INTRODUCTION

Carbenes are organic reactive intermediates with a neutral divalent carbon atom that is covalently bonded to two other substituents. Carbenes find a very useful application in polymer chemistry,¹ in the gas-phase combustion of organic and inorganic compounds,^{2,3} and in organic synthesis.^{4–7} The divalent carbon supports nearly isoenergetic electronic states of closed shell (singlet or spin-paired) and biradical (triplet) character, and the relative energy separation of these states is an important feature in understanding carbene reactivity. Being the smallest carbenes that exhibit closed shell ground states, the halocarbenes CXY (X = H, F, Cl, Br, and I; Y = F, Cl, Br, and I) have greatly contributed to our understanding of the reactivity of singlet carbenes and the factors that control the singlet-triplet energy gap.^{8,9}

In this study, we focus on the monohalocarbenes, CH(D)X.⁹ The lowest lying CHX singlet states ($\tilde{X}^1A'$ and $\tilde{A}^1A''$) are a well-known example of Renner-Teller coupled surfaces, since they result from a degenerate $^1\Delta$ electronic state at linear geometries.^{9–11} Lying energetically between the ground singlet state, $\tilde{X}^1A'$, and the first excited singlet state, $\tilde{A}^1A''$, is the triplet state, $\tilde{a}^3A''$, which couples with the singlet

states via spin-orbit (SO) coupling. Coupling of the triplet to the singlet ground $\tilde{X}^1A'$ state is important, as the states cross close to the minimum of each surface. This interaction was found to play a major role in the perturbation of vibrational levels of the interacting states,^{5,6,12–21} which has been examined in detail using laser-induced fluorescence (LIF), single vibronic level emission (SVLE) spectroscopy,^{22–32} and stimulated emission pumping (SEP) spectroscopy.^{33,34} While on one hand these studies have been remarkably successful in providing estimates for the singlet-triplet gaps, which have been compared with the predictions of *ab initio* and Density Functional Theory (DFT) calculations,^{18,35–60} and revealed perturbations of the singlet level structure by SO-coupling, which have been analyzed in some detail, on the other hand, a global analysis of the SO-coupling in these systems has not been performed. This is the goal of the present work.

The first approach employed here (*model 1*) uses a diabatic description, illustrated in Figure 1. Here, the potential curves of the singlet (S_0) and triplet (T_1) are illustrated to cross along a single critical coordinate that can be taken as the H–C–X bend, as the promotion of an electron from an in-plane sp^2 hybrid orbital to the out-of-plane carbon centered p -orbital results in reduced repulsion and an opening of the bond angle. Figure 2 shows a 2D surface plot of *ab initio* data as a function of R_{C-H} and the angle for the S_0 and S_1 states intersected by T_1 in CHCl. It is clear from Figure 2 that the bend is indeed

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: scott.reid@marquette.edu and dawesr@mst.edu

FIG. 1. Schematic diabatic one-dimensional picture of spin-orbit coupling in the halocarbenes. The spin-orbit coupling is factorized into a purely electronic part and a nuclear part reflecting the vibrational overlap of the singlet and triplet wavefunctions (*model 1*).

the relevant coordinate. For any particular pair of vibrational states, the magnitude of the SO-coupling will depend on the degree of vibrational overlap, and this is in fact consistent with the experimental observation that the bending vibrational levels of S_0 are the most perturbed. For example, in the case of CHI, the C–I stretching states are essentially unperturbed up to energies well above the triplet origin, while the lowest bending level is strongly perturbed, being shifted some 100 cm^{-1} from its predicted position by spin-orbit coupling. In this approach, we assume, then, that for any given singlet/triplet pair of interacting vibrational states, the SO-coupling matrix element can be written as follows:

$$\begin{aligned} \langle S_0(v_{S1}, v_{S2}, v_{S3}) | \hat{H}_{so} | T_1(v_{T1}, v_{T2}, v_{T3}) \rangle \\ = \mathcal{H}_{so}^{elec} \langle S_0(v_{S1}, v_{S2}, v_{S3}) | T_1(v_{T1}, v_{T2}, v_{T3}) \rangle, \end{aligned} \quad (1)$$

where $\mathcal{H}_{so}^{elec}$ is a purely electronic spin-orbit matrix element, and the integral on the right-hand side reflects the degree of overlap of the vibrational wavefunctions (and v_s and v_t are the singlet and triplet quantum numbers, respectively). Since several hundred of these matrix elements are required for even the smallest data set, this approximation allows one to use standard theoretical methods to accurately calculate the vibrational overlaps, with $\mathcal{H}_{so}^{elec}$ included as a single variable parameter. Support for this approach comes from previous studies on methylene (CH_2) by McKeller and co-workers¹⁹ where the SO-coupling matrix element between the ground electronic state ($\tilde{X}^3B_1$) and the first excited singlet electronic state ($\tilde{a}^1A_1$) was calculated over a range of bond angles using the Breit-Pauli Hamiltonian¹⁹ and found to vary by less than 20%.

To further test this assumption, a second model was applied (*model 2*). In *model 2*, SO-couplings were computed and fit into surfaces for appropriate coordinate ranges for each of the C(D)HX ($X = \text{Cl, Br, and I}$) systems. The geometry dependence of SO-coupling values was explored and indeed was found to vary most significantly with the angle coordinate. Some variation was also observed along R_{C-X} but almost none along R_{C-H} . This behavior is shown in the contour plots for CHI (Figure 3), which has the greatest magnitude of coupling. Numerous additional contour plots for all of the systems are provided as supplementary material.⁶¹ For *model 2*, the geometry dependent SO-coupling surfaces were used to compute coupling matrix elements without the approximation of Eq. (1). The matrix elements were evaluated by 3D numerical integration of the fitted SO-coupling surfaces over the vibrational wavefunctions of the singlet and triplet states (left side of Eq. (1)).

Using these two approaches, here, we report the results of global fits of SVL emission and SEP data for the halocarbenes

FIG. 2. 2D plot of lowest $1A'$ and $1A''$ states (S_0 and S_1 , solid color) with C–Cl distance fixed ($r_{\text{C-Cl}} = 1.6\text{ Å}$). The two singlets are degenerate for collinear geometries ($\text{Theta} = 180^\circ$) forming a Renner-Teller pair. The lowest $3A''$ triplet state (T_1 , transparent) cuts through S_0 not far from the minimum and is lower than the singlets for collinear geometries.

FIG. 3. Contour plots showing the geometry dependence of spin-orbit coupling values in CH(D)I. It can be seen that the coupling values (units of cm^{-1}) vary slightly with the R_{C-I} coordinate in addition to the bend, but negligibly with the R_{C-H} coordinate.

CH(D)X (X = Cl, Br, and I) which have (a) allowed many new assignments to be made, (b) provided improved experimental values for the singlet-triplet gaps for comparison with theoretical predictions, and (c) yielded detailed information on derived spin-orbit coupling constants. The latter are found to be strongly correlated with the measured constants of the corresponding halogen atoms and indicate significant quenching of the spin-orbit interaction. The SO coupling and other constants (e.g., singlet-triplet gap and anharmonic constants) from the global fits using the model described by Eq. (1) (*model 1*) are

compared with those obtained using the full matrix elements (*model 2*).

II. COMPUTATIONAL METHODS

There are many theoretical studies of the optimized geometries, vibrational frequencies, singlet-triplet gaps, and spin orbit coupling matrix elements in halocarbenes.^{35–60} Standard DFT methods such as B3LYP have been used to reliably calculate vibrational frequencies and equilibrium geometries, yet

few DFT methods accurately predict the singlet-triplet gap,^{59,62} which, however, is well reproduced by high level single reference (e.g., coupled-cluster with singles, doubles and perturbative triples [CCSD(T)]) and multi-reference methods such as multi-reference configuration interaction (MRCI) with suitable basis sets.

Our high-level explicitly correlated F12 calculations were done using the MOLPRO quantum chemistry program package.⁶³ Geometries were optimized for the lowest singlet (S_0) and triplet (T_1) surfaces of the halocarbene series CH(D)X (X = Cl, Br, and I) using the CCSD(T)-F12 and MRCI-F12 methods,^{64,65} correlating the valence electrons using the VQZ-F12 basis set.⁶⁶ Peterson's new pseudo-potential F12 bases were used for iodine and bromine.⁶⁷ Using those optimized geometries, singlet-triplet gaps were predicted at the VnZ-F12 and VnZ-PP-F12 levels ($n = 2-4$). Because we are interested in the vibrational overlaps, which in turn are sensitive to the geometries and force fields, we performed calculations of the vibrational frequencies and mass-weighted normal mode displacements (i.e., ℓ -matrices) with CCSD(T)-F12 and MRCI-F12 methods using the VQZ-F12 basis set. These modes were used to evaluate the full SO matrix elements used in *model 2* for one of the sets of global fits described below.

In addition, various DFT (B3LYP, M06, and M06-2X) and other post-Hartree-Fock (e.g., MP2) methods were tested for comparison. The differences in vibrational overlaps among these methods were relatively small, and the majority of results for *model 1* defined by Eq. (1) were obtained with the B3LYP functional in combination with an aug-cc-pVTZ or, in the case of iodocarbene, aug-cc-pVTZ-pp basis set. These calculations used the Gaussian 09 package on the Marquette University Pere cluster.⁶⁸

From these calculations, we extracted the structures, harmonic frequencies, and normal mode displacements to calculate the vibrational overlaps of the singlet and triplet state levels, incorporating the full effects of Duschinsky mixing⁶⁹ using a routine in the Pgopher program.⁷⁰ The vibrational term energies of the singlet and triplet states in the absence of spin-orbit coupling were assumed to follow separate Dunham expansion expressions of the form

$$G(v_1, v_2, v_3) = \omega_1^0 v_1 + \omega_2^0 v_2 + \omega_3^0 v_3 + x_{11}^0 v_1^2 + x_{22}^0 v_2^2 + x_{33}^0 v_3^2 + x_{12}^0 v_1 v_2 + x_{13}^0 v_1 v_3 + x_{23}^0 v_2 v_3, \quad (2)$$

where $\omega_1^0, \omega_2^0, \omega_3^0$ are harmonic frequencies for C–H stretch, H–C–X bend, and C–X stretch, respectively, v_1, v_2, v_3 are the associated vibrational quantum numbers, and x_{ij} are anharmonicity constants.

In *model 1* approach, the calculated harmonic frequencies were used as initial input with the calculated (product approximation) spin-orbit coupling matrix elements into an $n \times n$ Hamiltonian matrix, the diagonalization of which, carried out either in Excel or Matlab, yielded the eigenvalues and eigenvectors of the mixed singlet-triplet levels. All singlet and triplet state levels up to a threshold energy determined by the range of experimental data were included in this matrix. In order to fit these to the observed experimental values, we used as fit parameters $\mathcal{H}_{so}^{elec}$, the term energy of T_1 , the harmonic vibrational frequencies of S_0 and T_1 , and a limited set of an-

harmonicity constants. While $\mathcal{H}_{so}^{elec}$ should not vary for the two CH(D)X isotopomers, in this model, we fit it independently in order to assess the reliability of the approach.

For the second approach (*model 2*) using full SO-matrix elements, the SO couplings were computed at the MRCI-F12 level using VTZ-F12 and VTZ-PP-F12 basis sets and fit into surfaces which permit evaluation of SO-coupling matrix elements for comparison with the simpler model. The SO-couplings were all computed using the Breit-Pauli Hamiltonian in Molpro. The singlet and triplet states are of A' and A'' symmetry, respectively, and are connected by the X , Y , and Z components of the spin-orbit (LS) operator. All three S_z components of the triplet state couple to the singlet state (but not to each other). In Molpro, a symmetry adapted basis of the fine-structure states is constructed such that two triplet components couple to the singlet in a block of three components of A' symmetry. A second block of A'' symmetry contains only the other triplet component which is free of couplings. We further simplify the coupled A' block by constructing linear combinations of the two triplet components such that only one couples to the singlet, while the other does not. This results in a single real value that is fit into surfaces. The full information is contained in that single value since the eigenvalues in any of these matrix representations are the same.

The fits were used along with the wavefunctions to compute the SO coupling matrix elements as a part of a coupled Hamiltonian matrix which is otherwise the same as that of the first approach.

III. RESULTS AND DISCUSSION

Figure 4 shows the square of the calculated vibrational overlaps (i.e., the Franck-Condon factors or FCFs) of various S_0 vibrational levels with the T_1 origin in CHI, calculated at the MRCI-F12/VTZ-PP-F12 level. The FCFs are dominated by a single progression in the bending mode, $(0, n, 0)$, with a second progression $(1, n, 0)$ also observed. All other progressions, involving, for example, the pure stretching levels, have very small overlaps. This trend is noted in all carbene species studied.

FIG. 4. Calculated Franck-Condon factors describing the overlap of the T_1 origin with various S_0 levels in CHI at MRCI-F12/VQZ-F12 level. These calculations included the effects of Duschinsky mixing. The FCFs are largest for the pure bending levels, representing the single dominant progression.

TABLE I. Assignments of the observed energy levels for CHI. Energies are in cm^{-1} . Levels in italics are associated with the triplet state.

Energy level	Model 1 fit	Model 2 fit	Observed levels	Model 1 F-O ^a	Model 2 F-O ^a
(0,0,0)	0	0	0	0	0
(1,0,0)	589	585	591	-2	-6
(0,1,0)	955	954	948	7	6
(2,0,0)	1174	1182	1176	-2	6
(0,0,0)	1409	1400	1407	2	-7
(1,1,0)	1579	1587	1582	-3	5
(3,0,0)	1754	1758	1754	0	4
(0,2,0)	2069	2075	2070	-1	5
(1,0,0)	1971	1984	1975	-4	9
(2,1,0)	2215	2219	2218	-2	1
(4,0,0)	2329	2325	2326	4	-1
(2,0,0)	2583	2584	2584	-1	0
(1,2,0)	2705	2700	2704	1	4
(3,1,0)	2857	2843	2852	5	-9
(5,0,0)	2889	2891	2891	-3	0
(1,1,0)	3022	3021	3023	0	-1
(3,0,0)	3168	3174	3168	0	6
(0,3,0)	3270	3277	3275	-5	2
(2,2,0)	3335	3321	3330	5	-9
MAD^b				2.5	4.3

^aF-O—fit-observed.^bMAD—mean average deviation.

In describing our results, we will show in detail the results for CHI, while detailed results for the other carbenes are provided in the supplementary material.⁶¹ For CHI, a total of 19 levels derived from SVL emission data^{25,71} were included in the fit. Most of these levels were previously assigned and the present fit confirms the previous assignments that were made. As shown in Table I, the fits to 19 levels using *models* 1 and 2 resulted in mean average deviations (MAD) of 2.5 cm^{-1} and 4.3 cm^{-1} for *models* 1 and 2, respectively, which are of the order of the experimental uncertainty of $2\text{--}4 \text{ cm}^{-1}$.⁷¹ The two models differ in their flexibility. *Model* 1 is constrained by the constant (geometry independent) approximation to the SO-coupling, but at the same time, the magnitude of the SO-constant is flexible. In contrast, *model* 2 includes the geometry dependence in the SO-coupling, but the strength of the coupling was held to the computed *ab initio* values, fit as surfaces. It is also possible that the optimization procedure might exploit flexible parameters such as the anharmonic constants by varying them in an unphysical way. With this in mind, for *model* 1, as the spin-orbit matrix elements in this case are much larger than the anharmonicities, only x_{11} was deemed determinable. The fit returned a term energy for the triplet origin state of 1392.0 cm^{-1} , with $\mathcal{H}_{so}^{elec} = 731.5 \text{ cm}^{-1}$. The value for $\mathcal{H}_{so}^{elec}$ is within the range of values found on the fitted surface used for *model* 2. The complete set of optimized fit parameters are provided in Table S1.⁶¹ The derived harmonic frequencies (Table II) are generally in good agreement with the calculated values. All three methods (MRCI-F12, CCSD(T)-F12b, and B3LYP) predict C-I stretch frequencies on the singlet state close to the fitted values of the two models. The MRCI-F12 value for the bend on the singlet state is lower than the other calculations and fitted values. On the other hand, the MRCI-F12 value for the C-H stretch on the singlet is closer

to the B3LYP value and the fitted results from the two models than is the CCSD(T)-F12b value. For the triplet frequencies, the B3LYP value for the C-I stretch (643 cm^{-1}) differs most significantly from the fitted value of corresponding *model* 1 (616 cm^{-1}), while the other modes are in closer agreement. The results for MRCI-F12 and CCSD(T)-F12b for the CHI triplet frequencies agree closely with each other and the fitted parameters of *model* 2.

It is remarkable how much the modal character of the triplet state vibrations changes upon deuteration. The C-I stretch and the bend frequencies become close to each other in CDI, and the C-I stretch, which for the CHI isotopomer has very pure stretching character, mixes strongly with the bend mode. For the deuterated isotopomer, a total of 23 levels, again derived from SVL emission data,^{25,71} were fit to a MAD of 4.3 cm^{-1} using *model* 1. *Model* 2 returns a similar MAD of 4.6 cm^{-1} . A comparison of fit and observed levels is provided in Table S2 of the supplementary material.⁶¹ Again, the derived harmonic frequencies (Table II) are generally in excellent agreement with the calculated unperturbed predictions. Here, the fit returned a term energy for the origin of the triplet state of $1386(4) \text{ cm}^{-1}$, with $\mathcal{H}_{so}^{elec} = 731.0 \text{ cm}^{-1}$ for *model* 1 which is within the range of values used by the fitted surface in *model* 2. The complete sets of fit parameters for both models are provided in Table S1.⁶¹ The good agreement between the values of $\mathcal{H}_{so}^{elec}$ derived from independent fits to the data for the two isotopomers (731.5 cm^{-1} for CHI and 731.0 cm^{-1} for CDI) gives us confidence in the approach.

An analysis of the eigenvectors returned from the fits yields additional information on the strength and selectivity in coupling of the singlet and triplet levels. For example, in CHI, the eigenstate at 1754 cm^{-1} contains $\sim 93.7\%$ character of $S_0(3,0,0)$, indicating that this level is only weakly mixed with

TABLE II. Calculated and fit CHI and CDI vibrational frequencies in cm^{-1} .

Species	Mode	Calculated frequency 1 ^a	Calculated frequency 2 ^b	Calculated frequency 3 ^c	Model 1 fit frequency ^d	Model 2 fit frequency ^e
CHI (S ₀)	C–H stretch	2891.6	2935.6	2896.5	2841.0	2856.3
	Bend	955.76	1064.0	1050.0	1055.6	1045.9
	C–I stretch	599.5	606.3	587.8	573.7	594.3
CHI (T ₁)	C–H stretch	3192.9	3193.9	3131.8	3132.0	3192.9
	Bend	836.2	829.7	799.0	804.6	860.0
	C–I stretch	662.5	666.5	642.9	615.8	651.1
CDI (S ₀)	C–D stretch	2125.8	2155.5	2121.0	2060.5	2048.7
	Bend	701.8	785.6	775.0	793.2	798.8
	C–I stretch	588.1	593.0	574.0	564.6	563.3
CDI (T ₁)	C–D stretch	2350.0	2352.9	2314.8	2314.8	2324.6
	Bend	680.7	684.1	576.0	562.0	668.0
	C–I stretch	593.7	596.1	648.0	641.0	595.0

^aVibrational frequencies calculated at MRCI-F12/VQZ-F12 level.^bVibrational frequencies calculated at CCSD(T)-F12b/VQZ-F12 level.^cVibrational frequencies calculated at B3LYP/Sadlej-pVTZ level.^dModel 1 fit frequencies.^eModel 2 fit frequencies.

background triplet levels. In contrast, the level at 1582 cm^{-1} contains $\sim 72\%$ character of the triplet origin, indicating more significant mixing. This is consistent with our expectation (Figure 4) that levels containing bending excitation are the most strongly perturbed, due to their larger vibrational overlap with the triplet levels.

Turning to bromocarbene,²⁴ our initial studies of CHBr reported a fit of the observed singlet levels to a simple Dunham expansion,²⁴ which yielded a MAD of 16 cm^{-1} , significantly larger than our experimental uncertainty of $2\text{--}4\text{ cm}^{-1}$. This, of course, reflects the influence of spin-orbit coupling. Here, we fit a total of 38 CHBr levels observed by SVL emission to a MAD of 3.4 cm^{-1} using *model 1*, much improved and now on the order of our experimental uncertainty. *Model 2* returns a MAD of 5.7 cm^{-1} . A detailed line list is provided in Table S3 of the supplementary material,⁶¹ while Table S4

lists the derived fit parameters. Due to the smaller spin-orbit coupling, a larger (but still incomplete) set of anharmonicity parameters was used. The derived harmonic frequencies for CHBr and CDBr are shown in Table III for both the singlet and triplet electronic states. The agreement between the MRCI-F12 and CCSD(T)-F12b values and the results of *model 2* are particularly good for the triplet state. The MRCI-F12 method also performs well on the singlet, while the CCSD(T)-F12 value for the C–H stretch is significantly higher than the fitted value (*model 2*). The B3LYP values are in close agreement with the corresponding fit for *model 1* and also in rather close agreement with the MRCI-F12 results. The derived $\mathcal{H}_{so}^{elec}$ was 354.3 cm^{-1} , and triplet term energy is 2059.6 cm^{-1} using *model 1*, similar to that (2036.0) obtained using *model 2*. For CDBr, a fit to 41 levels derived from SVL emission spectra²⁰ resulted in a 3.2 cm^{-1} MAD and gave $\mathcal{H}_{so}^{elec} = 350.9\text{ cm}^{-1}$ and a triplet

TABLE III. Calculated and fit CHBr and CDBr vibrational frequencies in cm^{-1} .

Species	Mode	Calculated frequency 1 ^a	Calculated frequency 2 ^b	Calculated frequency 3 ^c	Model 1 fit frequency ^d	Model 2 fit frequency ^e
CHBr (S ₀)	C–H stretch	2845.2	2934.5	2881.0	2795.5	2809.9
	Bend	1090.7	1155.1	1147.0	1131.7	1135.0
	C–Br stretch	681.8	688.4	686.0	678.2	679.6
CHBr (T ₁)	C–H stretch	3198.4	3196.7	3147.0	3146.0	3184.3
	Bend	920.3	916.5	916.0	880.5	920.0
	C–Br stretch	748.3	751.9	747.0	755.0	740.5
CDBr (S ₀)	C–D stretch	2092.3	2154.5	2154	2074.1	2075.0
	Bend	802.7	856.5	853.7	844.2	840.0
	C–Br stretch	671.2	675.7	640.9	664.8	665.0
CDBr (T ₁)	C–D stretch	2354.3	2354.1	2336.0	2339.3	2345.0
	Bend	767.1	770.8	641.0	621.2	759.1
	C–Br stretch	658.2	659.4	732.5	716.9	650.0

^aVibrational frequencies calculated at MRCI-F12/VQZ-F12 level.^bVibrational frequencies calculated at CCSD(T)-F12b/VQZ-F12 level.^cVibrational frequencies calculated at B3LYP/aug-cc-pVTZ level.^dModel 1 fit frequencies.^eModel 2 fit frequencies.

FIG. 5. Energy level diagrams for CHBr in the region 3700–4900 cm^{−1} above the ground state using model 1 and model 2. Four sets of levels are shown: calculated S₀ levels without consideration of spin-orbit coupling (black, far left), calculated levels of primarily singlet character including the effects of spin-orbit coupling (green, middle left), observed levels (blue, middle right), and calculated levels of primarily triplet character including the effects of spin-orbit coupling (red, far right).

term energy of 2078.4 cm^{−1} using *model 1* and a MAD of 4.6 cm^{−1} and triplet term energy of 2063.4 cm^{−1} using *model 2*. Again, the consistency of the derived SO-coupling constants for the two isotopomers gives us confidence in the procedure.

To help visualize the nature of the spin-orbit coupling in this system, Figure 5 displays energy level diagrams for CHBr in the region 3700–4900 cm^{−1} above the ground state. Four sets of levels are shown: calculated S₀ levels without consideration of spin-orbit coupling (far left), calculated levels of primarily singlet character including the effects of spin-orbit coupling (middle left), observed levels (middle right), and calculated levels of primarily triplet character including the effects of spin-orbit coupling (far right). The shifts in level positions due to spin-orbit coupling are quite obvious, and typically large, on the order of tens of cm^{−1}. This figure also shows that while all singlet levels present in this region are in fact observed, only

a small fraction (here 2/6 = 33%) of the background triplet levels are observed experimentally.

Turning now to CH³⁵Cl, a (*model 1*) fit to 53 levels derived from SVL emission^{23,26} and SEP^{33,72} measurements yielded a MAD of 2.1 cm^{−1}, which is a more than twofold improvement over a simple Dunham expansion fit to the observed singlet levels. A fit using *model 2* does a similar job and returns a MAD of 2.0 cm^{−1}. The fit and observed energies are provided in Table S6 (supplementary material⁶¹), while Table S7 includes the fit parameters, which includes a nearly complete set of anharmonicity constants using both models. In this case, perturbations due to SO-coupling are of the same order of magnitude as the anharmonicities. The derived $\mathcal{H}_{so}^{elec}$ is 81.3 cm^{−1}, and *model 1* triplet term energy is 2167.8 cm^{−1}, which is very close to the value 2169.3 cm^{−1} obtained from *model 2*. Our *model 1* fit value of $\mathcal{H}_{so}^{elec}$ is centered in the

TABLE IV. Calculated and fit CHCl and CDCl vibrational frequencies in cm^{−1}.

Species	Mode	Calculated frequency 1 ^a	Calculated frequency 2 ^b	Calculated frequency 3 ^c	Model 1 fit frequency ^d	Model 2 fit frequency ^e
CHCl (S ₀)	C–H stretch	2868.2	2929.1	2917.4	2873.2	2873.0
	Bend	1218.3	1226.9	1228.2	1206.5	1205.7
	C–Cl stretch	819.7	826.1	792.6	815.6	815.3
CHCl (T ₁)	C–H stretch	3206.5	3201.8	3173.0	3076.4	3125.7
	Bend	974.6	970.8	952.8	958.8	959.3
	C–Cl stretch	891.9	897.45	874.8	883.5	886.1
CDCl (S ₀)	C–D stretch	2107.5	2148.8	2144.0	2119.2	2113.1
	Bend	904.9	914.2	908.9	896.7	897.3
	C–Cl stretch	809.2	817.7	784.7	805.7	806.3
CDCl (T ₁)	C–D stretch	2361.1	2359.8	2338.0	2333.7	2370.0
	Bend	889.3	898.8	710.2	698.9	907.2
	C–Cl stretch	724.1	725.6	869.4	884.7	710.0

^aVibrational frequencies calculated at MRCI-F12/VQZ-F12 level.
^bVibrational frequencies calculated at CCSD(T)-F12b/VQZ-F12 level.
^cVibrational frequencies calculated at B3LYP/aug-cc-pVTZ level.
^dModel 1 fit frequencies.
^eModel 2 fit frequencies.

range of fit values found on the surface used in *model 2*. Note that a previously reported calculated value (120 cm^{-1}) of Worthington and Cramer,⁵⁹ obtained at geometries near the seam of intersection using multi-reference configuration interaction methods, is significantly larger. The derived $\mathcal{H}_{so}^{elec}$ for CD^{35}Cl from a fit to 55 levels was nearly identical, 81.9 cm^{-1} . This underscores the strong correlation between the spin-orbit coupling and anharmonicities in the fit, due to the similarity of their magnitude. The least squares fitting of the calculated levels to the observed 55 CD^{35}Cl levels from SVL emission and SEP measurements returned a MAD of 1.7 cm^{-1} for *model 1* and 2.1 cm^{-1} for *model 2*. A complete line list is provided in Table S8 of the supplementary material,⁶¹ while Table IV gives the fit and calculated values of the harmonic constants. The MRCI-F12 and CCSD-F12 methods agree closely with each other and the fit in this case. Perhaps, the closer agreement between MRCI-F12 and CCSD-F12 for the CHCl system is due to the lack of effective core potential that was used to treat the Br and I containing systems. Both methods perform significantly better than B3LYP which produces some larger discrepancies.

With the fits for CH(D)X ($\text{X} = \text{Cl, Br, and I}$) completed, we are now in a position to examine periodic trends in the

data. Table V summarizes our findings on the singlet-triplet energy gaps. With the exception of CHI and CDI, the derived gaps are not substantially different from those previously estimated.⁹ The new value for CHI corresponds to a gap of 3.92 kcal/mol , or 16.42 kJ/mol using *model 2*, which can be compared with a variety of theoretical predictions. Toscano and co-workers predict a gap of 15.5 kJ/mol using the linear combination of Gaussian-type orbital-local spin density method.⁵³ Nguyen and co-workers predict a value of 18.8 kJ/mol at the $\text{CCSD(T)}/6\text{-}311++\text{G}(3\text{df},2\text{p})$ level,⁴⁶ which is of interest because the same level of theory underpredicts the gap in CHBr by $\sim 5\text{ kJ/mol}$. Other DFT calculations have been reported for CHI, which generally overestimate the gap.⁵⁹ Here, as listed in Table V, we obtain very similar values for the MRCI-F12 and CCSD(T)-F12b methods (15.5 and 15.2 kJ/mol , respectively). Both values are close to the experimental fit and the explicitly correlated CCSD(T)-F12b value is much closer than the previous standard CCSD(T) value of Nguyen. For CHBr and CHCl , comparing the experimental fit values with the calculated values in Table V, it appears that both explicitly correlated methods produce very accurate and reliable predictions, with the MRCI-F12 method slightly preferred.

TABLE V. Summary of the fit singlet-triplet energy gaps using *model 1* and *model 2* in cm^{-1} compared with those calculated using MRCI and CCSD(T) experimental data fit to models. Note: Since core-correlating basis was not available for Br and I, all electron calculations could not be performed on CHBr and CHI .

CHX singlet-triplet energy gap,		CDX singlet-triplet energy gap,	
Halogen atom X	ΔE_{ST}	ΔE_{ST}	Average ΔE_{ST}
I	1392.0	1394.8	1393.4
Br	2059.6	2078.4	2069.0
Cl	2167.8	2183.9	2175.9
CHX singlet-triplet energy gap,		CDX singlet-triplet energy gap,	
Halogen atom X	ΔE_{ST}	ΔE_{ST}	Average ΔE_{ST}
I	1372.5	1319.7	1346.1
Br	2036.0	2063.4	2049.7
Cl	2169.3	2175.7	2172.5
Calculated (CHI)			
Method/basis	VDZ-PP-F12	VTZ-PP-F12	VQZ-PP-F12
MRCI-F12	1244.9	1303.5	1294.7
CCSD-F12	1200.9	1272.1	1267.4
Calculated (CHBr)			
Method/basis	VDZ-PP-F12	VTZ-PP-F12	VQZ-PP-F12
MRCI-F12	1955.8	1991.2	1986.5
CCSD-F12	1931.7	1980.7	1987.4
Calculated (CHCl)			
Method/basis	VDZ-F12	VTZ-F12	VQZ-F12
MRCI-F12	2124.9	2175.9	2182.9
CCSD-F12	2078.6	2104.2	2111.7
Method/basis	CVDZ-F12	CVTZ-F12	CVQZ-F12
(AE) MRCI-F12	2164.6	2233.2	2250.0
(AE) CCSD-F12	1939.1	1950.5	1959.6

FIG. 6. Correlation of derived CH(D)X spin-orbit coupling constants (model 1) with the experimental values of the corresponding halogen atoms. A linear fit to the data is shown, which returns a slope of 0.144(2).

Figure 6 shows the correlation between the derived halocarbene spin orbit coupling constants and those of the corresponding halogen atom. A striking linear correlation is observed, which when fit with a fixed intercept of 0 yields a slope of 0.144(2). This indicates that in the halocarbenes, the spin-orbit coupling is significantly quenched with respect to the corresponding halogen atom. It also helps to explain why spin-orbit perturbations were not observed in our studies of fluorocarbene³⁴—the predicted $\mathcal{H}_{so}^{elec}$ in this case is ~ 40 cm⁻¹.

IV. CONCLUSIONS

In this work, a global analysis of spin-orbit coupling in the monohalocarbenes CH(D)X (X = Cl, Br, and I) is reported. Energies and anharmonic frequencies for the lowest singlet (S_0) and triplet (T_1) surfaces of the halocarbene series H(D)CX (X = Cl, Br, and I) have been computed at the MRCI-F12, CCSD(T)-F12, and B3LYP levels with basis set as large as the VQZ-F12 and VQZ-PP-F12. The magnitudes and geometry dependences of the spin-orbit couplings were explored. The couplings were computed and fit into surfaces which permit evaluation of SO-coupling matrix elements. This permitted a comparison between two models. First (model 1), within a diabatic treatment which separates the spin-orbit matrix elements into a purely electronic contribution and a nuclear component representing the vibrational overlap of the singlet and triplet wavefunctions, we treated the former as a fit parameter, while the latter was calculated using results from electronic structure theory. These were incorporated in a least squares fit to experimental data from SVL emission and SEP experiments. For model 2, the full spin-orbit matrix elements were evaluated by integrating over the fitted surfaces. In all cases, for both models, the mean average deviation was comparable to the experimental uncertainty, and this work has resulted in a number of new assignments, together with improved estimates of the singlet-triplet gaps and the first global experimental information on the spin-orbit coupling constants. The derived $\mathcal{H}_{so}^{elec}$ from model 1 show a good correlation with those of

bare halogen atoms, with the atomic spin-orbit coupling is quenched to about 14% in the halocarbenes.

ACKNOWLEDGMENTS

S.A.R. acknowledges funding of this work by the National Science Foundation (Grant Nos. CHE-1057951, CHE-0717960, and CHE-0353596 to S.A.R. and Grant No. CHE-1300945 to R.D.).

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