Angewandte Chemie

Dihalomethane Structures

A Dramatic Spin–Orbit Effect Observed in the Vibrational Frequencies of the Chloroiodomethane Cation**

*Mina Lee, Hyoseok Kim, Yoon Sup Lee, and Myung Soo Kim**

Several theoretical studies have suggested that a spin–orbit-induced isomer may be found for a molecule of the as-yet-unknow superheavy element 118, that is, $(118)F_4$,[1] but there have been no reports of an experimentally observed molecule for which the inclusion of spin–orbit effects is essential for the correct identification of the ground state structure. We report here a molecular ion, $[CH_2ClI]^+$, for which spin–orbit interactions are crucial for the identification of the structure and vibrational frequencies of the correct ground state. Theoretically, the spin–orbit interaction is part of the relativistic effect. The importance of relativity for the description of heavy atoms is well recognized.[2] Scalar relativistic effects are routinely included in electronic-structure calculations of molecules containing heavy elements through the use of relativistic effective core potentials (RECP), but spin–orbit interactions are usually omitted when deriving optimized structures partly because of the assumption that their influence on the molecular structures is negligible and partly due to computational difficulties. Even when spin–orbit terms are available in RECPs, the usual treatment involves perturbational inclusion of these terms after the variational determination of orbitals and structures. Quantum chemical calculations employing RECPs and spin–orbit operators from the start have been available for some time.[3] The spin–orbit density functional theory (DFT) method available in NWChem is particularly useful for the present purpose of demonstrating spin–orbit effects on geometries since the geometry can be optimized with both electron correlations and spin–orbit interactions included.[4]

We have been investigating the reactivity of mixed dihalomethane cations for some time. Hence, we have recorded the vibrational spectra of the cations by mass-analyzed threshold ionization (MATI) spectrometry.[5] Figure 1 shows the MATI spectrum of CH_2ClI recorded by monitoring $[CH_2{}^{35}ClI]^+$ in the electronic ground state. The most intense peak at around 78644 cm^{-1} corresponds to the 0–0 band. The distance of each peak from the 0–0 band in this spectrum corresponds to the vibrational frequency of the cation. CH_2ClI has nine nondegenerate normal modes: modes 1–6, with a' symmetry, and modes 7–9, with a'' symmetry. All the fundamentals and overtones of the totally symmetric modes, a', are dipole-allowed, while only the even-numbered overtones of the a'' modes are allowed. Utilizing the selection rule and the frequencies in the neutral species,[6] plausible assignments can be made for the prominent peaks; these are listed in Table 1. Modes 2 and 3 are due to CH_2 motion, modes 4 and 5 are C−Cl and C−I stretchings, respectively, and mode 6 is I−C−Cl bending. Other peaks in the spectrum are due to overtones and combinations.

Our normal routine is to perform quantum chemical calculations for the vibrational frequencies, isotope shifts, and Franck–Condon factors to confirm, improve, or revise the phenomenological assignments. In particular, results from the DFT/B3LYP calculations have been found to be adequate in most cases.[5] When we performed DFT/B3LYP calculations for $[CH_2ClI]^+$ with Gaussian 98, using a well-known RECP for iodine such as LanL2DZ,[7] we always obtained two distinct stationary states, $^2A'$ and $^2A''$, formed by removal of an electron from in-plane and out-of-plane iodine nonbonding orbitals, respectively. Even though their energies are nearly the same, their geometries are noticeably different because of the partial antibonding characteristics contained in essentially iodine nonbonding orbitals. The vibrational frequencies in the two states are also noticeably different, suggesting that the observed spectrum would be a superposition of two spectra.

The fact that a rather straightforward phenomenological assignment of the MATI spectrum was possible is not compatible with the calculated results. Moreover, the experimental frequencies could not be correlated with the calculated results with the accuracy expected for the DFT/B3LYP results (± 15 cm^{-1}). We thought that neglecting the spin–orbit effect could be one possible cause of this discrepancy, and we therefore performed the spin–orbit DFT calculations implemented in NWChem for neutral and cationic CH_2ClI in the electronic ground states using RECPs with the effective spin–

---

[*] M. Lee, Prof. M. S. Kim
National Creative Research Center for Control of Reaction Dynamics
and School of Chemistry, Seoul National University
Seoul 151-742 (Korea)
Fax: (+82) 2-889-1568
E-mail: myungsoo@plaza.snu.ac.kr
H. Kim, Prof. Y. S. Lee
Department of Chemistry and
School of Molecular Science (BK21), KAIST
Daejeon 305-701 (Korea)

[**] This work was financially supported by CRI, the Korea Research Foundation (KRF-2004-041-C00161), the Ministry of Science and Technology, the Brain Korea 21 Projects awarded to Seoul National University and KAIST, the Ministry of Education, and CNMM of KIMM, Republic of Korea. M.L. thanks the Ministry of Education for a Brain Korea 21 fellowship.

DOI: 10.1002/ange.200463090

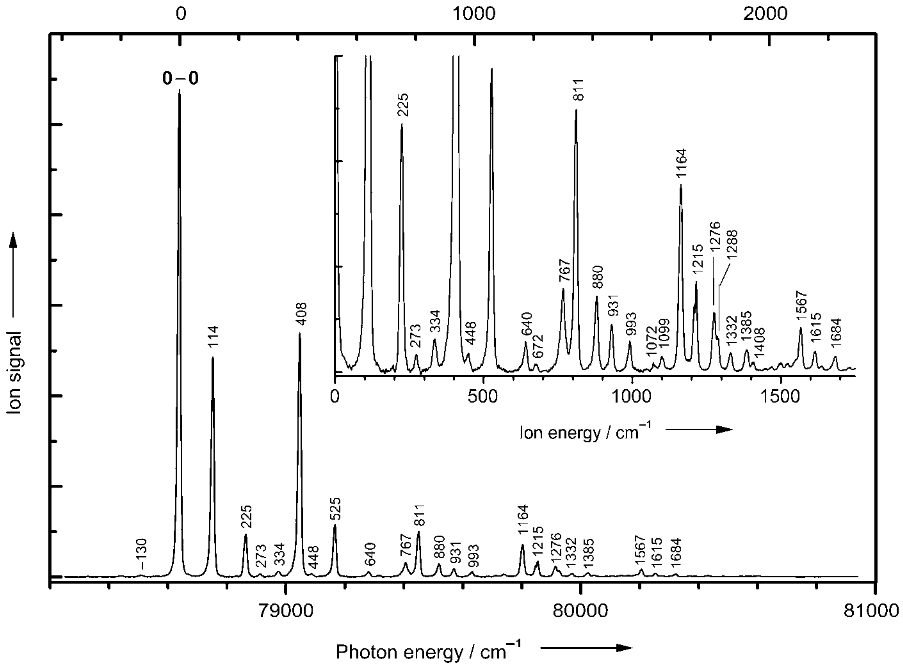

Figure 1. One-photon MATI spectrum of CH_2ClI recorded by monitoring $[CH_2{}^{35}ClI]^+$ in the electronic ground state. The *x* scale at the top corresponds to the vibrational frequency scale for the cation. Its origin is at the 0–0 band position. The spectrum in the 0–1700 cm^{-1} region magnified by 10 along the *y* axis is shown as an inset.

Table 1: Experimental vibrational frequencies [cm^{-1}] of CH_2ClI and $[CH_2ClI]^+$ in the electronic ground state and calculated data without (w/o) and with (w) the spin–orbit effect.[a]

Mode[b]		CH_2ClI			$[CH_2ClI]^+$		
		w/o S.O.	w S.O.		w/o S.O.		w S.O.
	exp.[c]	$^1A'$	^1A	MATI	$^2A'$	$^2A''$	^2A
1	3001	3126	3126	–	3132	3044	3106
2	1412	1439	1439	1385	1434	1382	1420
3	1188	1202	1202	1164	1169	1168	1175
4	740	707	709	767	726	726	747
5	536	523	518	408	507	359	419
6	192	188	186	114	163	180	112
7	3066	3207	3207	–	3216	3103	3206
8	–	1128	1127	1072	1073	1098	1089
9	–	782	780	–	847	789	791

[a] Calculated at the B3LYP level using the RECP of ref. [8] for halogen atoms and aug-cc-pVTZ for other atoms. The spin–orbit term in the same reference was used when needed. [b] Mulliken notation. [c] Raman spectroscopic data taken from ref. [6].

orbit potentials reported in ref. [8] for the halogen atoms. The size of the basis set was increased until the basis-set dependence of the vibrational frequencies became less than 15 cm^{-1}. To determine the importance of the spin–orbit terms, all the calculations were done with and without the spin–orbit potential but with the same RECP. The calculated equilibrium geometries of the neutral species and the cation have C_s symmetry. The optimized geometry of the neutral species is hardly affected by the spin–orbit terms (Table 2). For the cation, however, only one equilibrium geometry was obtained with the spin–orbit terms, instead of the two found in their absence. For the double group symmetry of the fine structure state in the presence of spin–orbit terms, both the ground and lowest excited states of the cation have the same symmetry. Unlike the DFT calculations without the spin–orbit terms, the spin–orbit DFT calculations did not locate the second state as the lowest fine-structure state. The second state is well separated, by about 4000 cm^{-1}, from the ground state.[9]

The most striking influence of the spin–orbit terms on the cation geometry (Table 2) is observed for the I–C–Cl bond angle. With the aug-cc-pVTZ basis set, these are 96.1° and 116.1° for $^2A'$ and $^2A''$, respectively, in the absence of the spin–orbit terms, and 106.0° in their presence. The trend observed in the vibrational frequencies (Table 1) is similar. The influence of the spin–orbit terms on the vibrational frequencies of the neutral is not significant, and the results are compatible with the experimental data. In the case of the cation, however, the two sets of frequencies calculated without the spin–orbit terms could not be correlated with the experimental data. The single set of vibrational frequencies obtained with the spin–obit terms, however, agrees well with the experimental data. For example, the I–C–Cl bending, mode 6, has the frequencies 163 and 180 cm^{-1} in $^2A'$ and $^2A''$, respectively, in the absence of the spin–orbit terms and 112 cm^{-1} in their presence; the experimental frequency is 114 cm^{-1}.

To the best of our knowledge, this is the first time that a dramatic spin–orbit effect has been observed for the vibrational frequencies and the shape of the ground state of a polyatomic molecule. The presence of an iodine atom is certainly a factor responsible for the above observation. Also important is the fact that two nearly degenerate electronic states with different geometries are present for the radical

Table 2: Bond length [Å] and angles [°] of CH_2ClI and $[CH_2ClI]^+$ in the electronic ground state without (w/o) and with (w) the spin–orbit effect.[a]

C_s		CH_2ClI		$[CH_2ClI]^+$		
		w/o S.O.	w S.O.	w/o S.O.[c]		w S.O.[d]
	exp.[b]	$^1A'$	^1A	$^2A'$	$^2A''$	^2A
C–I	2.137	2.181	2.187	2.187	2.243	2.242
C–Cl	1.774	1.778	1.777	1.767	1.716	1.738
C–H	1.062	1.081	1.081	1.082	1.090	1.084
I-C-Cl	112.5	114.4	114.4	96.1	116.1	106.0
H-C-I	108.3	106.6	106.6	109.6	101.0	104.9
H-C-Cl	108.4	108.6	108.7	111.9	112.9	112.7
H-C-H	111.0	112.1	112.0	115.8	111.8	114.5

[a] Calculated under the same conditions as in Table 1. [b] Microwave spectroscopic data taken from ref. [10]. [c] Two distinct stationary geometries with nearly the same energy appear in the absence of the spin–orbit term. [d] Only one stationary geometry is obtained in the presence of the spin–orbit term.

cation in the absence of the spin–orbit effect. The spin–orbit interactions lift this accidental orbital degeneracy by mixing two states strongly in the region connecting two minima.

The lack of experimental data displaying noticeable spin–orbit effects has been one of the justifications for ignoring its computational treatment even for molecules with quite heavy elements. The present results suggest that spin–orbit terms should be treated the same as other relativistic effects in some cases, and demonstrate unequivocally that accounting for the relativistic effect can be critical for the studies of radicals with heavy atoms. Also to be noted is that the calculated frequencies do not match the experimental results as well as in other systems reported previously,[3b] even when the spin–orbit terms are included, which implies that further refinement and improvement are desirable for the treatment of relativistic effects in open-shell systems. The present data provide a useful benchmark in the computational treatment of the relativistic effect. Preliminary studies indicate that the spin–orbit effect is important for other cations with an iodine atom.

Experimental Section

The vacuum ultraviolet (VUV) radiation generated by four-wave mixing in Kr was overlapped with the CH_2ClI molecular beam to excite the neutral species to their Rydberg states. These were ionized by an electric field pulse applied after a time delay. Measuring the molecular ion current as a function of the VUV wavelength gives the MATI spectrum, which is essentially a vibrational spectrum of the molecular cation.

Received: December 29, 2004

Keywords: density functional calculations · dihalomethanes · spin–orbit coupling · structure elucidation · vibrational spectroscopy

---

[1] a) C. S. Nash, B. E. Bursten, *Angew. Chem.* **1999**, *111*, 115; *Angew. Chem. Int. Ed.* **1999**, *38*, 151; b) Y.-K Han, Y. S. Lee, *J. Phys. Chem. A* **1999**, *103*, 1104.

[2] a) P. A. Christiansen, W. C. Ermler, K. S. Pitzer, *Annu. Rev. Phys. Chem.* **1985**, *36*, 407; b) P. Pyykko, *Adv. Quantum Chem.* **1978**, *11*, 353; c) Y. S. Lee, A. D. McLean, *J. Chem. Phys.* **1982**, *76*, 735.

[3] a) Y.-K. Han, C. Bae, S.-K. Son, Y. S. Lee, *J. Chem. Phys.* **2000**, *112*, 2684; b) Y. J. Choi, Y. S. Lee, *J. Chem. Phys.* **2003**, *119*, 2014.

[4] High Performance Computational Chemistry Group, *NWChem, A Computational Chemistry Package for Parallel Computers*, Version 4.1, Pacific Northwest National Laboratory, Richland, Washington, USA, **2003**..

[5] a) S. T. Park, S. K. Kim, M. S. Kim, *Nature* **2002**, *415*, 306; b) M. Lee, M. S. Kim, *J. Chem. Phys.* **2003**, *119*, 5085; c) M. Lee, M. S. Kim, *J. Phys. Chem. A* **2003**, *107*, 11401.

[6] V. Sablinskas, P. Klaeboe, C. J. Nielsen, D. Sülzle, *Analyst* **1992**, *117*, 365.

[7] Gaussian 98 (Revision A.6), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**..

[8] a) L. F. Pacios, P. A. Christiansen, *J. Chem. Phys.* **1985**, *82*, 2664; b) L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, W. C. Ermer, *J. Chem. Phys.* **1987**, *87*, 2812.

[9] I. Novak, J. M. Benson, A. W. Potts, *Chem. Phys.* **1986**, *107*, 129.

[10] I. Ohkoshi, Y. Niide, M. Takano, *J. Mol. Spectrosc.* **1987**, *124*, 118.