Low energy electron energy-loss spectroscopy of C F 3 X ( X = Cl, Br )

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Low energy electron energy-loss spectroscopy of CF₃,X (X=Cl, Br)

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We report threshold electron energy-loss spectra for the fluorohalomethanes CF₃,X (X=Cl, Br). Measurements were made at incident electron energies of 30 and 100 eV in energy-loss range of 4–14 eV, and at scattering angles of 4° and 15°. Several new electronic transitions are observed which are ascribable to excitation of low-lying states as well as are intrinsically overlapped in the molecules themselves. Assignments of these electronic transitions are suggested. These assignments are based on present spectroscopic and cross-section measurements, high-energy scattering spectra, and ab initio molecular orbital calculations. The calculated potential curves along the C–X bond show repulsive nature, suggesting that these transitions may lead to dissociation of the C–X bond. The present results are also compared with the previous ones for CF₃H, CF₄, and CF₃I. © 2007 American Institute of Physics. [DOI: 10.1063/1.2424704]

I. INTRODUCTION

Freon and related halogen-substituted methane molecules CF₃,X (X=H, F, Cl, Br, I) are, in general, important industrial molecules with wide-ranging applications such as semiconductor etching, refrigerants, fire extinguishers, etc. These tetrahedronlike systems are of fundamental interest for studying halogen substitutional effects as well. However, it has been widely recognized that CF₃Cl and CF₃Br are responsible, via photochemical mechanisms, for the depletion of the earth’s ozone layer that protects our planet from the damaging effects of short wavelength solar radiation. Also CF₃H and CF₄ are strong greenhouse gases, and, therefore, must be replaced by the alternative compounds that have low global warming potentials. One possible replacement is CF₃I due to its weak C–I bonding. Thus, there are practical as well as fundamental interests in obtaining adequate spectroscopic information of the underlying electronic transitions for these fluorohalomethanes. Though these molecules have been investigated by a variety of techniques, the systematic study is less extensive in low-energy electron spectroscopy (EELS). The present work is concentrated with the electron impact excitation of the threshold electronic states of CF₃Cl and CF₃Br.

In low-energy electron impact spectroscopy, molecular transitions resulting from the transfer of energy from incident electrons to target molecules are not restricted by the optical selection rules. The low-momentum-transfer (high impact energy, low scattering angle) energy-loss spectrum is equivalent to the photoabsorption spectrum. The large-momentum-transfer (low impact energy, high scattering angle) spectra can reveal the presence of optically forbidden excitation. Thus, electron impact spectroscopy is a useful complement to conventional optical spectroscopy in the assignment of molecular electronic states.

In these regards, we will first briefly review the previous works in vacuum ultraviolet (VUV) and electron-impact spectroscopy on primarily CF₃Cl and CF₃Br. Photoabsorption spectra have been studied extensively by Doucet et al. for both CF₃Cl and CF₃Br in the energy range from 6.2 to 10.33 eV. Gilbert et al. and Doucet et al. obtained the VUV spectra for CF₃Cl and CF₃Br, respectively, in the region extended to 19 eV. Photoelectron spectroscopy using resonance lamps was also carried by Doucet et al. for CF₃Br above about 11 eV, and synchrotron radiation measurements by Bozek et al. for CF₃X (X=F, Cl, Br, I). Biehl et al. reported VUV and visible spectroscopy of CF₃X (X=H, F, Cl, Br) using fluorescence excitation and dispersed emission technique. Mason et al. extensively studied photoabsorption of CF₃X (X=Cl, Br, I) using ASTRID synchrotron source and compared with the results from electron spectroscopy.

In the electron-impact studies, zero-angle electron energy-loss spectroscopy for CF₃Cl was performed by King and McConkey at the impact energy of 500 eV and by Zhang et al. at the impact energy of 8 keV. Momentum-
transfer-resolved electron energy loss spectrum has given information on an unusually low-lying nondipole transition at 7.7 eV in CF₃Cl by Ying et al. In addition, their ab initio generalized oscillator strengths (GOS) and single-excitation configuration interaction calculations showed that this transition is consistent with an electronic excitation from the nonbonding lone-pair orbital on the Cl atom to the antibonding * or- ital leading to dissociation of the C–Cl bond. Chen et al. studied the HOMO of CF₃Cl by binary (e,2e) electron momentum spectroscopy. They calculated the position density and the result shows that the electron concentrates near the nucleus of the Cl atom implicating that this orbital is the chlorine’s lone-pair orbital. And the momentum density shows that the orbital is p type. Sunohara et al. measured absolute differential cross sections for elastic and vibrationally inelastic scattering of electrons from CF₃Cl and CF₃Br using a crossed-beam experiment in the energy range of 1.5–100 eV. In this report, we have examined systematically the energy-loss region from 3 to 18 eV for all the halofluoromethanes up to CF₄ at incident electron energies of 30 and 100 eV and at the scattering angles of 4° or 3° for CF₃H and CF₃I and 15°. The molecular orbital calculations have also elucidated the threshold nature of low-lying electronic states in this halofluoromethane series.

II. EXPERIMENT

The electron spectrometer used in the present work has been described in detail elsewhere and will be outlined only briefly here. The spectrometer consists of an electron gun with hemispherical monochromator, a molecular beam, and a rotatable detector (from 10° to 130°) with a second hemispherical system. A beam of molecules is crossed with a monoenergetic beam of electrons of fixed incident energy. At a particular scattering angle, electrons are detected having lost energies in the range from 3 to 18 eV. These energy-loss spectra are measured at the angles of 4° (or 3° for CF₃H and CF₃I) and 15° and for incident electron energies of 30 and 100 eV. For comparison purpose, an “optical absorption” type spectrum was taken using high-energy, low-angle conditions. A number of tube lenses in the spectrometer have been used for imaging and energy control of the electron beam, whose characteristics were carefully modeled by electron trajectory calculations. Both the monochromator and analyzer are enclosed in differentially pumped boxes to reduce the effect of background gases and to minimize any stray electron background. Overall resolution in all spectra was 25–35 meV full width at half maximum. The angular scale was calibrated to ±1.5° by noting the symmetry of elastic scattering about the true zero-degree point. The energy scale was calibrated to the He 19.367 eV resonance at 90°.

III. THEORY

The adiabatic potential energy curves for the CF₃Cl and CF₃Br molecules in their electronic X¹A¹ ground state were obtained at the density functional theory level. The three-parameter density functional of Becke was applied with the Lee, Young, and Parr correlation functions (Becke3LYP).
CF3Cl all 50 electrons were active exception in this comparison due to the molecular symmetry and to gain knowledge on their excited states. The core of the heavier Br atom was described by means of a pseudopotential, while a Gaussian basis set contracted to [3s3p2d1f] was employed for the seven valence electrons of bromine, hence reducing the number of active electrons in the CF3Br calculation to 40 (in case of CF3Cl all 50 electrons were active). In the equilibrium geometry, the CX distance is confirmed to be 1.78 and 1.95 Å for X=Cl and X=Br, respectively. The CF separation at the two different equilibrium geometries is very similar, however, 1.33 Å for X=Cl and Br, and maintains an almost constant difference of 0.015 Å for |CX| ranging between 1.5 and 2.5 Å. The behavior of the optimized bond angles X–C–F and F–C–F along the CX stretch coordinate is shown in Fig. 1(a), which demonstrates the shape elongation of the molecule when X changes from Cl to Br. Eigenenergies of the HOMO (6e) and LUMO (8a4) orbitals are plotted in Fig. 1(b). It is interesting to note the presence of the peak in the LUMO orbital energy for shorter |CX| distances, where the dipole moment of the molecule diminishes (the carbon atom is symmetrically shielded by the electronegative halogens). The sign of the LUMO eigenvalue becomes negative with the increase of |CX| distance, still quite before the equilibrium geometry is reached, which reflects the polar character of the actual CX bond (the dipole moments along the C3v symmetry axis are about 0.43 D for X=Cl and 0.64 D for X=Br).

Figures 1(c) and 1(d) show the adiabatic potential energy curves and the first excited state for CF3Cl and CF3Br, respectively. The ground-state potential energy well is substantially broader in case of CF3Br. The energies of the first excited state A in Figs. 1(c) and 1(d) were computed by the GAUSSIAN 03 single-excitation configuration interaction method. The potential energy curves correspond well to the HOMO-LUMO excitations [cf. the difference of E(X)−E(A) in Fig. 1]. We note that the first excited state is strongly repulsive along the dipole axis of the molecule, which suggests that the electron-impact excitation of either molecule could result in the formation of X− along with a simultaneous fragmentation of the CF3X molecule.

IV. RESULTS AND DISCUSSION

The energy-loss spectra of CF3Cl and CF3Br are presented together with other family of the fluoromethyl halides, i.e., CF3H, CF3I, and CF4 in Fig. 2, in order to stress the commonality of their transitions. Rydberg transitions are presented using term values from the quantum defect interpretation with the photoelectron spectroscopy data available. Moreover, to compare with the spectra at two different impact energies of 30 and 100 eV, the data were normalized to each other at the strongest peak in each spectrum. Therefore, no direct comparison of the intensities between two impact energies can be made.

The electron configurations of the ground electronic state (X1A1) of the fluoromethyl halides CF3X (X =H, Cl, Br, I), which has a tetrahedronlike geometry of C3v, are as follows:

\[(3a1)2(2e)4(4a1)2(5a1)2(3e)4(4e)4(5e)4(1a2)2(6a1)4 \text{ for CF3H,} \]
\[(3a1)2(2e)4(4a1)2(5a1)2(3e)4(6a1)2(4e)4(5e)4(1a2)2(7a1)2(6e)4 \text{ for CF3Cl,} \]
\[(3a1)2(2e)4(4a1)2(5a1)2(3e)4(6a1)2(4e)4(5e)4(1a2)2(7a1)2(6e)4 \text{ for CF3Br,} \]
\[(4a1)2(5a1)2(3e)4(6a1)2(4e)4(5e)4(1a2)2(7a1)2(6e)4 \text{ for CF3I.} \]

Also, under \(T_d\) symmetry of CF4, the following configuration is obtained for the ground state:
\[(1a1)^2(1t2)^6(2a1)^2(3a1)^2(2t2)^6(4a1)^2(3t2)^6(1e)^8(4t2)^6(1t1)^6 \text{ for CF4.} \]

All excitations from these shells appear to follow a Rydberg pattern and have been classified. These molecules have been of great interests since they enable us to follow the changes that occur in the electronic structure and transitions of fluoromethane and the halogen lone pairs as a function of substitution and to gain knowledge on their excited states.

Overviews in Fig. 2 show the systematic trend that the thresholds for the electronic excitation and the ionization are shifting to lower energies as replacing with heavier halogen atoms in the same molecular symmetry C3v. CF4 is somehow exceptional in this comparison due to the molecular symmetry of \(T_d\). Also, the \(l-s\) coupling interaction is dominating and then is observed clearly in the splitting of sharp structures for CF3I. The electronic excitation in these molecular systems, moreover, may be divided into two contributions, one from the CF3 component and the other from the substitution with a halogen atom. Of course, this substitution changes the actual molecular orbital. Therefore, molecular orbital calculation is needed to identify more precisely the observed spectra on the quantum chemical scheme. From a point of the molecular dissociation process, as mentioned above, the low lying triplet state is essential to produce the CF3 radical,
besides the energies required for the dissociation are getting lower along the substitution as observed in Fig. 2. Those low-lying states are, for the first time, systematically identified as shown in Fig. 2 for CF3Cl, CF3Br, and CF3I by the low energy electron impact spectroscopy at 30 eV.

The observations are summarized for each fluoromethyl halide as follows.

**A. CF3H**

Following the previous measurements for the higher impact energies of 400 eV as well as for the photoelectron spectroscopy, the peaks at 10.92 and 11.95 are assigned to 6a1→3s and 6a1→3p, and also the higher features at 12.58, 13.65, and 14.99 eV to 5e→3s, 5e→3p, or 4e→3s and 4e→3p transitions using term values, respectively. To compare CF3H with CF4, we recall the fluoromethane series CH3F, CH2F2, CHF3, and CF4 including CH4 (Refs. 15 and 16) and discuss the substitution effect of F atom from the CH4 molecule. The highest orbital in CH4 has the 1t2 symmetry of a carbon-hydrogen sigma bonding correlated only with the carbon 2p orbitals.17 Along the halogen substitution from CH4 to CHF3, however, the uppermost component of the orbital 1t2 changes to more or less carbon-fluorine pi-antibonding character. This trend is just that presented by the first band at 10.92 eV in CF3H, but which was observed at lower energy side around the same energies of ~9.42 eV in CH3, CH3F2, and CH2F2. Thus, in CF3H, the first two bands are assignable as 6a1→3s and 3p.

**B. CF4**

The EELS and photoelectron results show that all excitations from the ground state have been classified as Rydberg feature as shown in Fig. 2. The transitions of 1t1→3s and 1t1→3p or 5a1 correspond to the peaks at 12.6 and 13.7 eV, respectively. The two highest molecular orbitals, 1t2 and 4t2, are overlapped closely by 1.2 eV.15 The former transition is expected to have a symmetry forbidden character due to weak oscillator strength of 0.024±0.003. It is noted that the 1t1 orbital is composed of fluorine lone-pair pi orbitals, while 4t2 is carbon-fluorine sigma bonding. And, the latter transition indicates more or less carbon-fluorine pi-antibonding character due to HOMO→LUMO transition. The next higher features at 13.9 and 15.8 eV are assigned as the transitions of 4t2→3s and 4t2→4s, 3d or 1e→3p, respectively. The band at 14.8 eV is assignable as 1e→3s, indicating a forbidden transition because this band is clearly observed in more favorable experimental condition at 30 eV for 20° than at 100 eV for 4°.

**C. CF3Cl**

Figure 3 shows the electron energy loss spectra for CF3Cl at the impact energy of 30 eV and the scattering angle...
of 15° and at the impact energy of 100 eV and the scattering angle of 4°. Based on numerous results from the photoelectron and the dipole EELS measurements, in the valence-shell electronic structures of CF3Cl, the peaks at 9.6, 10.6, and 11.5 eV are assigned to 6e → 4s, 6e → 4p, 6e → 5s, 3d, respectively, and peaks 11.5 and 13.2 eV are also identified as 7a1 → 4s, 7a1 → 3d, 4d, 5s, respectively, terminating to the Rydberg limit of 7a1−1. 6e (HOMO) orbital is comprised essentially of a lone pair on Cl atom, and 7a1 is an orbital associated with C–Cl bonding. Therefore, the first ionization potential near 13.0 eV corresponds to taking out of one electron from the chlorine lone pair orbital, and the second ionization potential near 15.2 eV is related to the orbital populated in the C–Cl bond.2 As shown in Fig. 3, around 7.7 eV, the peak with a low-lying nondipole character is clearly emerged at the impact energy of 30 eV for the scattering angle of 15° but not at the impact energy of 100 eV for 5°. This nondipole electronic transition with a quadrupole characteristic is observed for the first time in the electron energy loss experiments. However, it was previously observed by the different experimental method using the momentum-transfer-resolved electron loss spectroscopy10 at 2.5 keV, which was assigned as 6e(HOMO) → 8a1(LUMO) transition related an electronic transition from a nonbonding Cl 3p orbital (HOMO) to an antibonding σC–Cl orbital (LUMO). In the case of nCl3p → σ∗ C–Cl transition, the overlap between the initial-state and final-state orbital wave functions occurs mostly at Cl site. The transition moment of this electronic transition is expected to resemble that of p-to-p transition in Cl atom which explains the quadrupole nature.10,18–20 In the study by Ying et al.,10 the GOS of this transition has been determined and found to have a shape characteristic of a quadrupole transition with a maximum at around 1 a.u. of the momentum transfer. While similar low-lying quadrupole transitions have been observed for other members of CFC, no such nondipole transition is found in the case of CF3, suggesting the involvement of Cl atoms in this quadrupole feature. The LUMO was found to be a repulsive potential character by McLean and Chandler.21

D. CF3Br

The electron energy loss spectrum for CF3Br is given in Fig. 4. As assigned previously from the UV spectrum data, the strong bands at 8.7 and 9.53 eV are associated with the Br 6e−1 ionization at 12.0 eV, the transitions from the bromine lone pair orbital to 5s and 5p terminating orbitals, respectively. The former one has a shoulder at 8.42 eV, which is due to spin-orbit splitting and there is no corresponding shoulder observed for CF3Cl, where this splitting is much clearer for CF3I than for CF3Br. The peak at 8.7 eV is a singlet-singlet transition and the shoulder at 8.42 eV has a singlet-triplet character.1 However, Eden et al.7 argue that the relative intensity of the two peaks at 8.42 and 8.7 eV are approximately equal in 100 eV, 4° and 30 eV, 15° spectra (see Fig. 2) and this lack of angular dependence strongly suggests that both features are due to singlet to singlet transitions. This leads Eden et al. to suggest that the broad feature peaked at 8.42 eV is due to the promotion of an electron from the second highest occupied molecular orbital (MO) (C–Br σ) to the LUMO (C–Br σ∗). The band at 10.54 eV corresponds to the transition of 7a1 → 5s. The first ionization potential corresponds to Br lone pair orbital, and the second ionization potential belongs to bonding orbitals of mainly C–Br character. Compared to CF3Cl, the ionization potentials of 6e and 7a1 for CF3Br are lower by around 1 eV.5 Though, as mentioned above, no direct comparison is possible in the intensity, the minimum and the peak positions are apparently changed in the spectral shapes around 9.53 eV due to the optical forbidden transitions involved strongly. The most prominent feature is a clear observation again for the low-lying electronic excitation states near threshold around 6.5 eV at electron impact energy only of 30 eV not of 100 eV. But, this feature is not mainly due to the optical forbidden character, like a triplet state, because the weak transition has been also observed in the vacuum ultraviolet spectrum.1

E. CF3I

The assignments for the transitions are reported previously (Ref. 6 and references therein). Briefly, the weak broad band observed around 4.6 eV was identified as 5pπ → σ∗ (C–I) transition which is composed in the 3Q1 (4.10 eV), 3Q0 (4.70 eV), and 1Q1 (5.34 eV) states due to the spin-orbit coupling and exchange interactions as confirmed by the photoabsorption results. The 3Q0 and 1Q1 states are enhanced at 4.70 and at 5.34 eV for the impact energy of 30 and 100 eV, respectively, as shown in Fig. 2. Moreover, the resultant excited states, i.e., the broad features without a fine vibrational progression, are leading to dissociation along the C–I stretch coordinate due to occupation of the C–I (2P3/2, 2P1/2) antibonding state, respectively, where 5pπ is the outermost lone-pair π orbital of I atom and σ∗ is antibonding carbon iodide sigma MO. The peaks at 7.13 and at 7.75 eV are assigned as

FIG. 4. Electron energy loss spectra of CF3Br in the energy-loss region from 4 to 14 eV at incident electron energies of 30 and 100 eV and at scattering angles of 15° and 4°, respectively.
6e_{3/2} \rightarrow 6s \text{ and } 6e_{1/2} \rightarrow 6s \text{ Rydberg transitions, giving rise to four components: } 2E_{3/2}[2], 2E_{3/2}[21], 2E_{1/2}[0], \text{ and } 2E_{1/2}[1] \text{ again due to the spin-orbit and exchange interactions. On those bonds with the bound state nature, the weak vibrational progressions are visible even with the present energy resolution of our spectrometer though the bands exhibit clearly structure dominated by the vibrational progressions in their high resolution photoabsorption spectra. The further bands being observed at 8.8 and 9.6 eV are tentatively attributed to the transition of } 6e_{3/2} \rightarrow 7s \text{ and } 6e_{1/2} \rightarrow 7s, \text{ and weak features observed between 8.5 and 8.6 eV may be due to a vibrational progression and the band between 9.1 and 9.4 eV due to excitation of yet another state. There is no information available for a series of the bands above 10 eV, and thus a full electronic structure calculation deriving the energies of high-lying Rydberg series would be desired.}

V. CONCLUSIONS

By varying the scattering angle and incident energy, we have studied systematically a low-lying transition in the valence shells of the halogen-substituted methane molecules CF_3X (X=H,F,Cl,Br,I). As mentioned above, those low-lying states are, for the first time, systematically identified for CF_3Cl, CF_3Br, and CF_3I by the low energy electron impact spectroscopy at 30 eV, in which the large-momentum-transfer (low impact energy, high scattering angle) spectra are, in general, favorable to detect the presence of optically forbidden excitations. Furthermore, including CF_4, these all four molecules have a lone-pair electron in each halogen atom, but not in the halogen atom of CF_3H. From the molecular-symmetry point of view, former three belong to C_3v, but CF_4 belongs to a different and much higher symmetry of T_d. Therefore, it is concluded that the halogenated CF_3Cl, CF_3Br, and CF_3I with C_3v symmetry as well as a lone-pair electron reveal the low-lying weak band, leading to dissociation of the molecules into the CF_3 radical along the C–X molecular axis. Furthermore, the CIS molecular calculation reveals the repulsive potential nature of LUMO for those two molecules, which supports the present experimental results. The direct product table for the symmetry group C_3v indicates that the 1a_1 → 1e transition is both dipole allowed and quadrupole allowed, and the small transition dipole moment therefore suggests that this transition can be attributed predominantly to quadrupole interactions. In addition, as indicated by the dominant molecular orbital coefficients, the 1a_1 → 1e transition corresponds to a transition from an essentially nonbonding Cl 3p orbital to an antibonding p–\sigma^* C–Cl orbital. The p-to-p transition is therefore consistent with a quadrupole transition. It should also be noted that a vertical transition originated from the ground vibrational level of the 1A_1 state terminates at the repulsive part of the potential energy curve of the 1E state above its dissociation limit.

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