Formation of excited fragments in the dissociation of halogenated methane compounds by electron impact

N. P. Danilevskiĭ, V. T. Koppe, A. G. Koval', and N. A. Khovanskiĭ

Khar'kov State University

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We measured the effective cross sections for the dissociation of halogenated methane compounds into excited fragments. The dependence of the cross section σ for the formation of the fragment $CH^*(A\,^2\Delta)$ on the binding energy E_b of this radical in the investigated molecule is obtained in the form $\sigma = A \exp(-kE_b)$, where $A = (8 \pm 1)\times 10^{-17}$ cm^2 and $k = 0.6 \pm 0.07$ eV^{-1}.

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The decrease of the cross section for the formation of the fragments $CH^*(A^2\Delta)$ and H^* with increasing number of particles in electron-dissociated molecules of complex hydrocarbons was attributed by Möhlmann and de Haar[1] and by Sushanin[2] to the increased number of possible dissociation channels, as well as to an increase of the internal-conversion probability. As shown in[3], however, another explanation of this experimental fact is possible, based on the dependence of the cross section of the dissociative excitation of the fragments on their binding energy in the dissociated molecule. Thus, the cross section of dissociative excitation of the fragment $CH(A^2\Delta)$ was shown in[3] to depend on the binding energy of this fragment in the molecule in the case of chlorinated compounds of methane. To ascertain whether this dependence is a general, we investigated other halogenated compounds of methane.

We report here an investigation of dissociative excitation of the molecules CH_2Br_2, $CHBr_3$, CH_3I, and CH_2I_2 by electrons with energies from 0.4 to 6 keV. The emission spectra of these molecules contain all the emissions present in the spectrum of the CH_4 molecule,[4] plus an appreciable number of lines of BR I, BR II, I I and I II. The Balmer-series lines of hydrogen are overlapped by the halogen lines. All the measurements were performed in the single-collision region. The experimental setup and the procedure for measuring the excitation cross sections were described earlier.[5]

Table I shows the measured cross sections for dissociative excitation of the fragment $CH^*(A^2\Delta)$ at an electron energy $E = 4$ keV. It shows also the results of[3] for chlorinated methane compounds and the binding E_b of the CH radical in the molecule.

The energy E_b was calculated in the following manner: It was assumed that the C–H, C–Cl, C–Br and C–I binding energies of all the molecules investigated here[6] do not depend on the number of hydrogen atoms and halogen atoms in the molecule, while the binding energy of the CH radical in the molecule is equal to the sum of the corresponding binding energies that must be broken to obtain the free fragment CH. Thus, the binding energy of the fragment CH in all molecules is equal, apart from a constant equal to the excitation energy of the $A^2\Delta$ state of the CH radical, with the minimal energy of the dissociation process that leads to the formation of the fragment $CH^*(A^2\Delta)$, while all other fragment atoms are in the ground state.

TABLE I.

Molecule	$\sigma \cdot 10^{21}$ cm^2 CH $(A^2\Delta)$	E_b, eV	Molecule	$\sigma \cdot 10^{21}$ cm^2 CH $(A^2\Delta)$	E_b, eV
CH_4	99	11.1	CH_2Br_2	452	8.6
CH_3Cl	139	10.5	$CHBr_3$	872	7.4
CH_2Cl_2	223	9.8	CH_3I	401	9.3
$CHCl_3$	480	9.1	CH_2I_2	836	7.4

It is seen from Table I that the dissociative-excitation cross sections of the fragment $CH(A^2\Delta)$ increase on going to molecules with lower binding energy of the CH radical. Figure 1 shows a plot of $\sigma[CH(A^2\Delta)]$ against the binding energies of the CH radical in the molecules. It is seen from this figure that the cross section for the formation of the $CH^*(A^2\Delta)$ fragment depends exponentially on the binding energy of this fragment in the investigated molecules and can be represented by the formula

$$\sigma = A \exp(-kE_b). \tag{1}$$

The values of the coefficients are for this case $A = (8 \pm 1) \times 10^{-17}$ cm^2 and $k = (0.6 \pm 0.07)$ eV^{-1}.

Using this formula, we can calculate the dissociation cross sections of other halogenated methane compounds with production of $CH(A^2\Delta)$, which are difficult to measure for one reason or another. Thus, for example, for the molecules CH_3F, CH_2F_2, CHF_3, CH_3Br and CHI_2 the

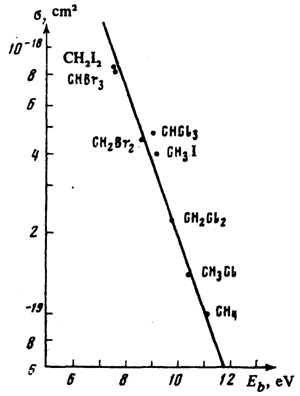

FIG. 1. Dependence of $\sigma[CH(A^2\Delta)]$ on E_b of the CH radical in a molecule.

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TABLE II.

λ, Å	Transition	$\sigma\cdot10^{21}$ cm^2			
		CH_2Br_2	$CHBr_3$	CH_3I	CH_2I_2
4479	Br I, $5s^4P-6p^4D^0$	8.3	18.0		
4706	Br II, $5s^5S^0-5p^5P$	72.0	120		
4818		28	55		
5056	Br II, $4d^3D^0-5p'^3F$	19.0	43.0		
5332	Br II, $4p^{53}P^0-5p^3P$	34.5	62.0		
5586	Br II, $5p'^3P-5d'^3P^0$	16.0	24.0		
4917	I I, $6s^4P-7p^4P^0$			13	30
4454	I II, $6p^5P-6d^5D^0$			12	28
4629	I II $6p'^3D-7sc^0$			13	22
4668	I II, $6p^5P-6d^5D^0$			26	63
5163	I II, $6s^5S^0-6p^5P$			87	210
5247	I II, $6s'^3D^0-6p'^3P$			14	53
5409	I II, $6s'^3D^0-6p'^3D$			34	88
5627	I II, $6s^3S^0-6p^3P$			25	86

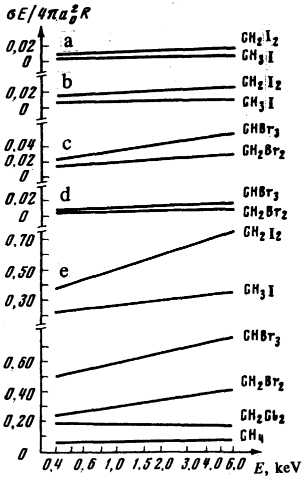

FIG. 2. Dependence of $\sigma E/4\pi a_0^2 R$ on E of a number of emission lines of the halogens and of the fragment CH (E is in logarithmic scale): a—for I II, λ = 5163 Å; b—for I I, λ = 4918 Å; c—for Br II, λ = 5332 Å; d—for Br I, λ = 4479 Å; e—for the fragment CH($A^2\Delta$–$X^2\Pi$).

cross sections for the formation of $CH^*(A^2\Delta)$ at an electron energy 4 keV are found from (1) to be respectively 6×10^{-20}, 3.7×10^{-20}, 2.3×10^{-20}, 2×10^{-19}, and 2.63×10^{-18} cm^2, respectively.

Table II lists the dissociative-excitation cross section of a number of most intense lines of Br I, Br II, I I, and I II. Altogether, approximately 30 lines of Br I and Br II and about 60 lines of I I and I II are observed reliably in the spectral region investigated by us. The lines were identified using the well-known handbook.[7] Just as for the Cl II lines,[3] the cross sections increase almost constantly with increasing number of the halogen atoms. In the case of chlorinated methane compounds, the excitation cross sections of the chlorine lines increase by ~2.5 times on going from CH_3Cl and CH_2Cl_2 and by 2.3 times on going from CH_2Cl_2 to $CHCl_3$.[3] The dissociative excitation cross sections of the lines Br I and Br II are approximately doubled on going from CH_2Br_2 to $CHBr_3$, and those for I I and I II increase by 2.6 times on going from CH_3I to CH_2I_2. The growth of the excitation cross sections of the lines of the halogen atoms in the investigated molecules may be partly due to the increase in the number of molecule-dissociation processes with fragment formation.

In the present study we measured the excitation functions of the fragment $CH^*(A^2\Delta)$ and of a number of multiplets of the halogen lines in the electron energy interval 0.4–6 keV; the results are shown in Fig. 2 in the form of plots of $\sigma E/4\pi a_0^2 R$ against $\ln E$, where σ are the excitation cross sections of the corresponding fragment, E is the electron energy, a_0 is the Bohr radius, and R is the Rydberg energy. The same figure shows for comparison the corresponding plots for CH_4 and CH_2Cl_2.[3] It is known[8,9] that at sufficiently high electron energies the plot of $\sigma E/4\pi a_0^2 R$ against $\ln E$ is a straight line with a positive slope when the main contribution to the formation of the excited fragment is made by dipole transitions, and a line with zero slope when the fragments are produced upon dissociation of states that are symmetry-forbidden relative to the ground state of the parent molecule. It is seen from Fig. 2 that the contribution of the dipole transitions to the $CH^*(A^2\Delta)$ formation increases with decreasing binding energy of the CH fragment in the investigated molecule. From the obtained dependences of $\sigma E/4\pi a_0^2 R$ on $\ln E$ for $CH^*(A^2\Delta)$ we determined the square of the matrix element of the dipole transitions (M^2) that contribute to the formation of the $CH^*(A^2\Delta)$ fragment, namely: 0.0087 (CH_4); 0.065 (CH_2Br_2); 0.091 ($CHBr_3$); 0.058 (CH_3I); and 0.14 (CH_2I_2). It is seen also from Fig. 2 that an appreciable contribution is made by the dipole transitions to the formation of excited halogen atoms and ions.

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