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MASS-SPECTROMETRIC STUDY OF CESIUM HALIDES

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Until recently, there was no information on the association of molecules in cesium halide vapors; it was assumed that the vapors consisted only of diatomic CsX molecules. However, in 1958 Milne, Klein, and Kubitschek (^{1}), and also Berkowitz and Chupka (^{2}), using a mass spectrometer, found that upon electron ionization of cesium chloride vapor, ions Cs_2Cl^+ are formed in relatively small amounts, indicating the presence in the vapor of dimeric Cs_2Cl_2 molecules. Eisentstadt, Rothberg, and Kusch (^{3}), who studied the velocity distribution in molecular beams of alkali-metal fluorides, found the ratio of the pressures of dimer and monomer in cesium fluoride vapor at $T = 863^\circ$K, $p_d/p_m = 0.093$, and the heat of dissociation of dimeric molecules into monomers, $\Delta E_T = 37.8 \pm 1.3$ kcal/mol. In 1959, Schoonmaker and Porter (^{4}), by the mass-spectrometric method, determined differences in the heats of dissociation of dimeric molecules of alkali-metal fluorides and, taking for sodium fluoride a heat of dissociation $\Delta H_T = 60.0$ kcal/mol (^{5}), obtained the value of the heat of dissociation of the cesium fluoride dimer $\Delta H_T = \Delta E_T + RT = 41.4 \pm 3.7$ kcal/mol ($T = 1121^\circ$K).

In a study of the free evaporation of alkali-metal halides, Rothberg, Eisentstadt, and Kusch (^{6}) found slight dimerization of molecules in cesium bromide vapor ($p_d/p_m \leqslant 0.04$); for the iodide, dimerization was not detected (somewhat earlier Miller and Kusch (^{7}) estimated the possible upper limit of the ratio of dimer and monomer pressures in cesium chloride and bromide vapors as 0.05 and 0.08, respectively). Thus, quantitative data are available only for cesium fluoride. It was therefore of interest to carry out a mass-spectrometric study of all cesium halides in order to determine the composition of the vapor and to measure the heats of dissociation of the dimeric molecules.

The work was carried out on an MS-4 mass spectrometer. An ion source with a double effusion chamber was used. The substance under investigation was placed in the lower chamber; effusion of vapor took place from the upper chamber, connected to the lower one by a narrow channel. Separate heating of the chambers made it possible to vary the temperature of one of them while leaving the temperature of the other constant. Part of the molecular beam emerging from the upper chamber was subjected to electron ionization. A more detailed description of the apparatus is given

Table 1

Mass spectra of cesium halides

Substance	T-re, °K	Cs^+ (I_0)	CsX^+ (I_1)	Cs_2X^+ (I_2)	$I_2/(I_0+I_1)$
Cesium fluoride	793	100.0	0.00	8.30	0.083
Cesium chloride	828	100.0	1.43	6.23	0.061
Cesium bromide	829	100.0	7.21	5.81	0.050
Cesium iodide	787	100.0	25.9	4.00	0.032

earlier ([8]). Table 1 gives the mass spectra of cesium halide vapors obtained under the following operating conditions of the instrument: accelerating voltage 1.5 kV; cathode emission current 1.0 mA; ionizing voltage 90 V. The intensities of the ion currents were summed over all isotopic varieties; the intensities of the weak ion currents X^+ and Cs_2^+ are not indicated. The mass spectra were recorded at the same temperature of the upper and lower chambers; therefore the data of Table 1 correspond to saturated vapors.

In all spectra the ion currents Cs_2X^+ were recorded, which indicates the presence of dimeric molecules Cs_2X_2 in the vapors. In order to take into account, in determining the heats of dissociation and the vapor composition, the mutual superposition of the spectra of monomers and dimers, the intensity ratios in the spectra of cesium fluoride and chloride dimers were found. For this purpose, measurements of the ion currents were carried out at a constant temperature of the upper chamber T_2 as a function of the temperature of the lower chamber T_1. Thus, the equilibrium constant of the dissociation reaction of dimeric molecules (in the upper chamber)

$$Cs_2X_2 \rightleftharpoons 2CsX \tag{1}$$

remained unchanged during the experiment, while the total pressure and, consequently, the degree of dissociation changed. Using the formulas given in ([8,9]), the following ratios were obtained from these measurements for cesium fluoride: $I_{02}/I_2 = a_{02} = 0.7 \pm 0.3$; $I_{12}/I_2 = a_{12} = 0.00$; for the chloride: $a_{02} = 0.6 \pm 0.2$; $a_{12} = 0.04 \pm 0.01$. Here I_{02} and I_{12} are those parts of the ion currents I_0 (Cs^+) and I_1 (CsX^+) which are due to their origin from ionization of dimeric molecules. For cesium bromide and iodide, in the subsequent calculations the value of the coefficient $a_{02} = 0.6$, found in experiments with the chloride, was used.

Measurements of the heats of dissociation of dimeric molecules were carried out as follows: the maximum overheating of the upper chamber relative to the lower one was established; then, at constant temperature of the lower chamber T_1, the temperature of the upper chamber T_2 was lowered. Measurements of the ion currents were made at intervals of approximately 10°; after reaching the point of equal temperatures ($T_1 = T_2$), the temperature of both chambers was further lowered, maintaining $T_2 \leq T_1$. The course of the change in the intensities of the ion currents I_0, I_1, and I_2 as a function of T_2 is shown in Fig. 1.

The heats of dissociation of dimeric molecules were calculated from the temperature dependence of the quantity $K^* = I_{01}^2/I_2$, proportional to the equilibrium constant of reaction (1). Here $I_{01} = I_0 - a_{02}I_2$ is the ion current of Cs^+ from the monomer. The results of the calculations are given in Table 2. Data from one of the experiments

Table 2

Heats of dissociation of dimeric molecules and vapor composition of cesium halides

Molecule	Temp., °K	ΔE_T, kcal/mole	p_d/p_m
Cs_2F_2	704—859	36.4 ± 0.9	0.14 (793°K); 0.11 (813°K)
Cs_2Cl_2	745—875	32.4 ± 1.3	0.07 (810°K); 0.07 (828°K)
Cs_2Br_2	786—909	31.2 ± 0.6	0.05 (826°K); 0.03 (829°K)
Cs_2J_2	755—862	31.2 ± 0.1	0.03 (787°K); 0.04 (820°K)

with cesium chloride are presented in Fig. 2. The heat of dissociation of the cesium fluoride dimer found by us agrees, within the experimental error, with the literature data (^{3,4}); the heats of dissociation of the dimeric molecules of cesium chloride, bromide, and iodide have been obtained for the first time.

The experimental data for determining the heats of dissociation (up to the point $T_1 = T_2$) were used to calculate the ratio of the vapor pressures of the monomer and dimer p_d/p_m by the method proposed by Milne (^{10}). It was used

a calculation formula derived taking into account the molecular flow of vapor through the channel connecting the upper and lower chambers (^{8}):

$$p_\mathrm{d}/p_\mathrm{m} = \frac{I_2}{I_{01}\sqrt{T_2}} \cdot \frac{I'_{01}\sqrt{T'_2} - I_{01}\sqrt{T_2}}{I_2\sqrt{T_2} - I'_2\sqrt{T'_2}}. \tag{2}$$

Here I_{01} and I_2 are the intensities of the ion currents of the monomer (Cs^+) and dimer (Cs_2X^+) at the point of equal temperatures of both chambers ($T_1 = T_2$); I'_{01}, I'_2 are the intensities of the same ion currents at the point $T'_2 > T_1$. The

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

method gives the relative composition of the saturated vapor at the temperature $T = T_1 = T_2$. The results of the calculations are given in Table 2. Since, for cesium halides, the heats of dissociation of dimeric molecules are smaller than the heats of sublimation of monomers, the ratios $p_\mathrm{d}/p_\mathrm{m}$ should increase with increasing temperature. Deviations from this regularity observed among the data of Table 2 are due to errors in determining the quantities $p_\mathrm{d}/p_\mathrm{m}$.

Fig. 1. Curves of the dependence of the logarithms of ion currents on reciprocal temperature, cesium chloride:
1 –Cs^+; 2 –$(\mathrm{CsCl}^{35})^+ \cdot 100$;
3 –$(\mathrm{Cs_2Cl}^{35})^+ \cdot 100$.

Fig. 2. Dependence of $\lg K_c^*$ on $1/T$, cesium chloride.

Let us consider the relation between the intensities of ion currents in the mass spectra of cesium halides and the composition of their vapor. The ions Cs^+ and CsX^+ are formed predominantly upon ionization of CsX molecules, which predominate in the vapor; the ion current $I_2(\mathrm{Cs_2X^+})$ amounts to about one half of the total ion current upon ionization of $\mathrm{Cs_2X_2}$ molecules. With satisfactory accuracy it may be assumed that the ratio of ionization cross sections of dimeric and monomeric molecules is close to two. Taking these circumstances into account, we arrive at the conclusion that the value of the ratio $I_2/(I_0 + I_1)$ should be close to the value $p_\mathrm{d}/p_\mathrm{m}$. Comparison of the data of Tables 1 and 2 confirms this conclusion. Thus, from the ratio of ion currents one can determine the relative composition of the vapor if the spectra of its components are known.

In experiments with cesium chloride, attention was drawn to the fact that the ratio of ion currents I_0/I_1 ($\mathrm{Cs^+/CsCl^+}$) decreases with increasing temperature, irrespective of whether the relative concentration of dimeric molecules in the vapor decreases or increases (see Fig. 1). Consequently, the course of the ratio I_0/I_1 depends only weakly on the contribution of the dimer to the ion currents Cs^+ and CsCl^+, and is determined mainly by the temperature dependence of the mass spectrum of the monomer, which can be traced more accurately from the ratio of the ion currents Cs^+ and CsCl^+ of the monomer: $I_{01}/I_{11} = a_{01}$ ($I_{11} = I_1 - a_{12}I_2$). In the interval of 100°, a_{01} changes from 86 (800° K) to 67 (900° K), i.e., by more than 20%. Thus, in the present case, as the temperature increases the probability of formation of molecular ions CsCl^+ increases, which can be explained by considering the mutual arrangement of the potential

energy of the CsCl molecule and the CsCl^+ ion. From the fact of the low intensity in the mass spectrum of molecular CsCl^+ ions in comparison with the fragment ions Cs^+, it follows that r_c—the "critical" distance of the molecular ion at which its energy is equal to the dissociation energy—noticeably exceeds r_e, the abscissa of the minimum of the potential-energy curve of the CsCl molecule.

As the temperature is raised, the population of the upper vibrational levels increases. Molecules occupying these levels are more likely to be at internuclear distances $r > r_c$. Therefore, upon electron impact, transitions leading to the formation of stable molecular ions occur more often.

In the case of cesium bromide and, especially, cesium iodide, the relative intensities of molecular ions in the mass spectra are considerably higher, which indicates a smaller difference between r_c and r_e than for the chloride. Therefore, an increase in the population of the upper vibrational levels has only a weak effect on the number of molecules that form molecular ions upon electron impact. In addition, the population of the upper levels of CsBr and CsJ molecules increases more slowly with increasing temperature, since their vibrational constants are smaller than that of cesium chloride (CsCl, $\omega_e = 209$ cm^{-1}; CsBr, $\omega_e = 139$ cm^{-1}; CsJ, $\omega_e = 101$ cm^{-1} ([11])). For the reasons indicated, the temperature coefficients of the spectra of cesium bromide and iodide are close to zero.

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CITED LITERATURE

[1] T. A. Milne, H. M. Klein, D. Cubicciotti, J. Chem. Phys., **28**, 718 (1958).
[2] J. Berkowitz, W. A. Chupka, J. Chem. Phys., **29**, 653 (1958).
[3] M. Eisenstadt, G. M. Rothberg, P. Kusch, J. Chem. Phys., **29**, 797 (1958).
[4] R. C. Schoonmaker, R. F. Porter, J. Chem. Phys., **30**, 283 (1959).
[5] R. F. Porter, R. C. Schoonmaker, J. Chem. Phys., **29**, 1070 (1958).
[6] G. M. Rothberg, M. Eisenstadt, P. Kusch, J. Chem. Phys., **30**, 517 (1959).
[7] R. C. Miller, P. Kusch, J. Chem. Phys., **25**, 860 (1956).
[8] P. A. Akishin, L. N. Gorokhov, L. N. Sidorov, *Vestnik MSU*, ser. mathematics, mechanics, astronomy, physics, chemistry, No. 6, 194 (1959).
[9] L. N. Gorokhov, *Vestnik MSU*, ser. mathematics, mechanics, astronomy, physics, chemistry, No. 6, 231 (1958).
[10] T. A. Milne, J. Chem. Phys., **28**, 717 (1958).
[11] S. A. Rice, W. Klemperer, J. Chem. Phys., **27**, 573 (1957).

Note: Figure translations are in progress. See original paper for figures.