Manifestation of interference of quasimolecular states in the mass spectra of complex molecules

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The conditions under which oscillations of the cross sections for dissociative ionization of complex molecules by electrons or by light can be observed are discussed on the basis of the model of Rosenthal and Foley. One of the possible versions of observation of such effects is realized in experiment. It is shown that the cross sections for the formation of R^+ and $GeBr_3^+$ ions by electron impact oscillate in antiphase in the $RGeBr_3$ compound sequence.

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Investigations of atomic collisions reveal occasionally oscillations of the total cross section of the inelastic channels as a function of the collision energy.[1-4] This phenomenon was explained within the framework of the theory of nonadiabatic transitions[5] on the basis of the three-level quasimolecule model proposed by Rosenthal and Foley.[1]

A similar model can be used to describe the dissociation of a diatomic molecule excited into a dissociating state by electron impact or by light. For example, Papernov and Yanson[6] have shown that the photodissociation of Na_2 is accompanied by nonadiabatic transitions induced by the radial motion of the atoms. For a clear proof that the dissociation proceeds nonadiabatically, it is of interest to simulate in the molecule-dissociation process the atomic-collision conditions that permit observation of the oscillation of the total cross section in one of the decay channels. This is of particular interest for polyatomic molecules. To this end it is necessary to be able to vary the velocity at which the fragments of the molecule pass through a region where the terms come together or cross, with the region located at a large distance from the equilibrium position. This is possible in the case of dissociative ionization of complex molecules. For example, dissociative ionization of certain molecules is so rapid that there are no molecular ions in the mass spectrum.

For such compounds, the decay of the molecular ion can be reminiscent of the decay of a diatomic molecule: the decay proceeds with breaking of one bond in one oscillation. In the breaking of one and the same bond, it is possible to vary the kinetic energy of the fragments by changing the energy of the ionizing electrons or photons.[7] It is possible to change the mass of the fragments and preserve approximately the kinetic energy if the fragment mass does not influence the character of the terms corresponding to the broken bond. Then, with a favorable combination of the dimensions of the loop encircled by the interfering terms,[5] and the rate of dispersal of the fragments, one can expect the appearance of oscillations of the total dissociative-ionization cross section, e.g., as a function of the energy of the photons (electrons), or in a series of compounds of the same type dissociating along one bond.

In this study we have attempted to observe oscillations of the total cross section for dissociative ionization by electron impact in a series of compounds of the same type. The choice of the compounds is determined by the requirements for simulating the conditions of observation of the oscillation of the total cross section of the elastic channels in atomic collisions: 1) the molecular ion RX^+ must not be present in the mass spectrum; 2) the mass spectrum must constitute a superposition of the mass spectra of $R^{\cdot}$ and $X^{\cdot}$, which is evidence in favor of single-channel decay of $RX^{+\cdot}$ along the R–X bond and facilitates the determination of the total cross section for dissociative ionization of RX along one of the channels

$$RX+e\rightarrow R^{+}+X^{\cdot}+2e, \tag{1a}$$

$$RX+e\rightarrow R^{\cdot}+X^{+}+2e; \tag{1b}$$

3) the system of terms corresponding to the broken bond does not depend on the nature and consequently also on the mass of R or X; 4) terms of the systems $(R^{+}X^{\cdot})$ and $(R^{\cdot}+X^{+})$ should be close to one another, i.e., the ionization potentials of $R^{\cdot}$ and $X^{\cdot}$ must not differ greatly.

We have shown[8] that the mass spectrum of $C_4H_9GeBr_3$ satisfies well the first two requirements, being practically the sum of the mass spectra of $C_4H_9^{\cdot}=R^{\cdot}$ and $GeBr_3^{\cdot}=X^{\cdot}$. At the same time it is known that the electron influence along the carbon chain in n-hydrocarbons is transmitted over not more than 4–5 CH_2 links,[9,10] so that one can hope the molecular-ion term system corresponding to a broken Ge–C bond to be identical for all compounds of the type $C_nH_{2n+1}GeBr_3$ with $n>4$–5. In dissociative ionization of these compounds it is possible, with practically no change of the character of the terms of the quasimolecular state through which the molecular ion that dissociates in accord with the scheme (1a), (1b) passes, to vary the rate of dispersal of the fragments by going from one state to another and maintaining constant the energy of the ionizing electrons. The ionization potentials of the normal alkyl radicals with $n>4$ (~8 eV) and $GeBr_3^{\cdot}$ (8.5 ± 0.5 eV) are also close.[11] Thus, compounds of the $C_nH_{2n+1}GeBr_3$ sequence turn out to be convenient objects with which to simulate the conditions for the observation of the oscillations of

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the total cross section of the inelastic channels in atomic collisions.

We synthesized $RGeBr_3$ compounds with $R = C_4H_9$, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, and C_9H_{19} by the procedure described in Ref. 12, and plotted their mass spectra. We used a standard MKh1303 mass spectrometer with a thermostatic unit for direct insertion of the samples; the construction of the spectrometer is described in Ref. 13. The character of all the mass spectra coincides fully with the character of all the mass spectrum for $C_4H_9GeBr_3$ described above. For each compound, the mass spectrum was plotted three times, and we calculated the averaged quantities

$$Q_1=\frac{\sum\limits_i I(R_i^+)}{I_0},$$

which are proportional to the cross section for dissociative ionization along the channel (1a), as well the quantities

$$Q_2=I(\mathrm{GeBr_3^+})/I_0,$$

which are proportional to the cross section for dissociation along the channel (1b). Here $\sum_i I(R_i^+)$ is the sum of the intensitites of all the hydrocarbon peaks in the mass spectrum of the given compound; $I(\mathrm{GeBr_3^+})$ is the intensity of the $GeBr_3^+$ peak; I_0 is the sum of the intensities of all the peaks in the mass spectrum of the same compound.

The variation of the quantities Q_1 and Q_2 in the sequence of the investigated compounds is shown in Fig. 1. The error bar for Q_1 is equal to the mean squared error of the corresponding Q_1. The errors of Q_2 do not exceed the geometric dimensions of the points. It is seen that Q_1 oscillates. The connecting lines are drawn purely for illustration, since in measurements of this kind it is impossible to investigate the behavior of Q for fractional values of n.

The cross section for dissociative ionization along the channel (1b) also oscillates in the investigated sequence of compounds, but in antiphase with Q_1, as expected. If it is assumed in accordance with the postulate that the terms along the Ge–C bond are identical, then in all the investigated cases the kinetic energy T of the diverging particles (R and $GeBr_3$) is the same, and it is possible to calculate for each compound the value of $1/v$ in units of $T^{-1/2}$, where v is the relative velocity of the fragments during the first stage of the decay of $C_nH_{2n+1}GeBr_3^+$. The results of such calculations are:

n:	4	5	6	7	8	9
$1/v$:	4.91	5.38	5.78	6.14	6.45	6.72

It is seen from these results and from the figure that the last four points are approximately equidistant and are apparently close to the position of the extreme of the oscillating function $Q_1 = f(1/v)$. The same holds true also for Q_2. Thus, the character of the oscillations of Q_1 and Q_2 agrees with that expected on the basis of the model of Rosenthal and Foley, and we have apparently succeeded in simulating the conditions for observation of the oscillations of the total cross sections of the inelastic channels in ion-atom collisions. We can then conclude with respect to the mechanism of dissociative ionization of the $RGeBr_3$ molecules that the molecular ion $RGeBr_3^+$ decays rapidly at least through two channels, whose terms come close together (or cross) at relatively large distances, and the states corresponding to them interfere.

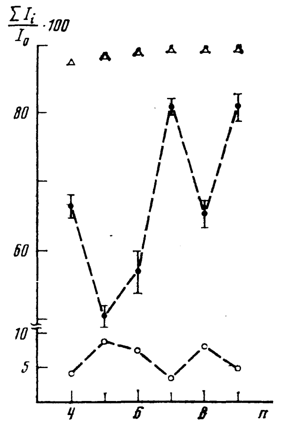

FIG. 1. Variation of the cross section for dissociative ionization via a selected channel in a sequence of compounds of the same type under electron impact: ●—cross section for the production of the ion $C_nH_{2n+1}^+$ from $C_nH_{2n+1}GeBr_3$ (Q_1); ○—cross section for the production of the ion $GeBr_3^+$ from $C_nH_{2n+1}GeBr_3$ (Q_2); Δ—cross section for the production of the ion $C_nH_{2n+1}^+$ from $C_nH_{2n+1}I$ (Q_1).

It should be noted that the limited possibility of choosing the points on the $1/v$ scale in the method used by us to identify nonadiabatic transitions in dissipative ionization processes should lead in the general case only to a distortion of the monotonicity of the experimentally determined values of Q in the sequence of the employed compounds. If, however, the position of the employed compounds coincide on the $1/v$ scale with the position of the inflection points of the oscillating function $Q = f(1/v)$, then the monotonicity will not be violated at all, even in the presence of interference between the states. Therefore the "good" behavior of Q_1 and Q_2 in our result is accidental. The behavior of $C_5H_{11}GeBr_3$ deviates from the general sequence. This can be attributed to the fact that up to this compound the influence of the character of R on the position of the terms corresponding to the broken bond is still felt. This should disturb the regularity of the oscillations in the investigated sequence of compounds.

To observe the oscillations it is apparently also important that the ionization potentials of the radicals produced in the decay differ little. For example, alkyl iodides RI and $RGeBr_3$ are almost identical. However, the corresponding quantities in the mass spectra vary monotonically in the same sequence $R = C_4H_9$–C_9H_{19}, as illustrated in Fig. 1 for Q_1. In this case X = I. The terms of the final states are strongly separated in this case: the ionization potential of iodine is 10.45 eV.[11]

This, however, is more readily a methodological than a fundamental factor, inasmuch as in the mass spectra of RBr (Ref. 14) (the ionization potential of bromine is 11.84 eV, Ref. 11) an irregularity of Q_1 is observed in the corresponding series of compounds.

This may be an indication in the favor of participation of nonadiabatic transitions in the dissociative ionization also in alkyl hadides. In this case, however, there should be interference between the state that correlates with $R^{\cdot}+Br^{+}$ or $R^{\cdot}+I^{+}$, on the one hand, and the state that correlates with $R^{+\cdot}+Br^{\cdot}$ or $R^{+\cdot}+I$, on the other, where $R^{+\cdot}$ is the electronically excited carbonium ion. The population of the state correlating with $R^{+\cdot}+Br(I)$ will determine in fact the magnitude of the effect. On the other hand, it is important that Q_1 and Q_2 be comparable, otherwise additional experimental difficulties will be encountered in the registration of the oscillations. At a large difference between the ionization potentials of the fragments, in accordance with the Stevenson rule,[15] the charge will be localized practically on one fragment, and the experimental registration of the oscillations of $Q_1(Q_2)$ in this case is analogous to the problem of registration of weak signals against a large background. In the case of the mass spectra of RBr, the irregularities in the cross section for the production of the ion Br^{+}, which would be in antiphase with the irregularities in the production of the ion R^{+}, cannot be observed. This is possibly connected just with the very weak intensity of the Br^{+} ions in the mass spectra of alkyl bromides.[14]

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