vation are not present in cases a) and b).

In conclusion, we discuss briefly the effect of external fields on the P-odd effects in the transitions $1s_{1/2}-2p_{1/2}$ and $2s_{1/2}-2p_{3/2}$. If a random electric field D is present in the experiment, then it also mixes states of opposite parity. The amplitude of such a transition A_D must not exceed the amplitude of the basic transition $A_p(A_0)$. If there is also present a random magnetic field H, then the interference between A_D and $A_p(A_0)$ leads to the appearance of effects simulating nonconservation of parity. For $H=0$ due to the interference between A_D and $A_p(A_0)$ a polarization vector $\mathbf{P}' \parallel \mathbf{n}\times\mathbf{D}$ appears but it is orthogonal to the polarization $\mathbf{P} \parallel \mathbf{n}$ brought about by the weak interaction. In the case of the transition $1s_{1/2}-2p_{1/2}$ we have for the configuration a) the following restrictions: $D \leqslant D_0 = 10^{-2}$ V/m, $H \ll 3\times10^{-2}\, D_0/D$ G. For the configuration b) in this transition $D \lesssim D_1 \sim 10^{-3}$ V/cm, $H \ll 3\times10^{-2}\, D_1/D$ G. For the transition $2s_{1/2}-2p_{3/2}$ the restrictions on the external fields have the form $D \leqslant D_2 = 1$ V/cm, $H \ll 2\times10^{-5}\, D_2/D$ G.

In a field $H=10^3$ G the levels $2s_{1/2}$ and $2p_{1/2}$ cross[11] and the magnitude of P-odd effect is increased by a factor of approximately 5 as a result of the increase in δ. However in this case it is apparently not possible to utilize this increase since there appears an induced electric field $\mathbf{D}=\mathbf{v}\times\mathbf{H}$. In the case of realistic values of $v \sim 10^{-5}$ $D \sim 2$ V/cm and $A_D \sim 10^3 \times A_p$, $A_D \sim 10\, A_0$.

The authors are grateful to V. G. Gorshkov and A. I. Mikhaĭlov for valuable discussions.

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Chemical radiative collisions

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A new type of elementary atomic collision event, namely, chemical radiative collisions, is examined. In each such event, the absorption (emission) of a photon is accompanied by a chemical reaction. A special case, namely, the substitution of an inert-gas atom R for a halogen atom in a molecule X_2 is analyzed. This process is accompanied by an optical transition of the quasimolecule RX_2 from a covalent to an ionic term. The associated light absorption coefficient is very large: it amounts to ~ 1 cm^{-1} for densities $N_{X_2} \sim N_R \sim 3\times10^{19}$ cm^{-3}. In strong fields with amplitudes $E_0 \sim 10^7$ V/cm, the cross section for such chemical radiative collisions may be up to ~ 100 Å^2 and, at still higher light intensities, it ceases to depend on E_0. The results of the first experiments in this field are reported. Measurements of the absorption coefficient and of the corresponding wavelength range are found to be in agreement with theoretical predictions. Possible applications of the effect are discussed.

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1. We have investigated chemical reactions between molecules during collisions in a light field. In these previously unexplored reactions, which we shall refer to as "chemical radiative collisions" (or, briefly, chemical RC), the field participates not in the preparation of the states of the colliding particles X and Y, but in the elementary event itself. In general, a radiative collision (RC) is commonly understood to mean an elementary event in which a photon is emitted (or absorbed) during the collision, so that the conservation of energy can be satisfied during an inelastic transition of the XY molecule. By chemical RC we shall understand events in which the result of the application of the light field is that the collision produces not only a change in the structure of the electron shells of the colliding particles[1–6] but, in addition, the atoms form new bound states, i.e., a chemical reaction occurs during the collision. The simplest example of chemical RC are the well-known photoassociation and photodissociation reactions:

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$$A+B+\hbar\omega\rightleftharpoons AB^*,\quad A+B^*\rightleftharpoons AB+\hbar\omega. \tag{1}$$

The various bimolecular chemical RC of the form

$$X+Y+\hbar\omega\rightarrow Z+U, \tag{2}$$

where X, Y, Z, U are the colliding molecules, are quite new and interesting.

We shall confine our attention to the probably simplest chemical RC defined by (2), where the collision of a diatomic molecule and an atom results in the photosubstitution reaction

$$A+BC+\hbar\omega\rightarrow AB+C. \tag{3}$$

2. It is well known that analysis of radiative collisions can be reduced to the usual collision theory formalism. Thus, the analysis of the transitions is performed for the so-called "compound system," i.e., a quantum-mechanical object consisting of the colliding particles and the field.[1,3,6] When nonlinear effects connected with the interaction between the fields and the colliding particles are neglected, the set of terms of this compound system splits into two groups, namely, terms belonging to the quasimolecule itself (0) and terms that have been raised (depressed) along the energy scale by the amount $\hbar\omega$, i.e., one quantum of energy (ω). This is illustrated in Fig. 1 which shows a number of terms for the simplest case, i.e., the compound system $AB+\hbar\omega$. The terms of group (0) and group (ω) can cross when the frequency ω is suitably chosen. Such crossing points determine the separation between the nuclei of atoms A and B, for which the $i\rightarrow f$ transition between the initial i and final f states of the compound system occur in accordance with the Franck-Condon principle. The corresponding $i\rightarrow f$ transition determines the absorption (emission) of a photon during a radiative collision.

In the case of complicated chemical radiative collisions, the terms of the quasimolecule and of the compound system are potential surfaces in multidimensional space in which the atomic configurations are specified. Instead of crossing points, we have multidimensional crossing curves. This complicates the discussion of chemical radiative collisions in a general form. Moreover, the Franck-Condon principle imposes a strong limitation on the choice of chemical radiative collisions that are of interest for practical realization. Let us consider this in greater detail by taking the example of photosubstitution (3). To realize this reaction, the atom A must be brought close enough to the molecule BC for the configuration of the quasimolecule ABC to correspond simultaneously to the B–C bond and the repulsion of A in the initial state i, and the bond A–B and the repulsion of C in the final state f. If the substitution reaction does not proceed in the absence of the light field (and this is the case that is interesting for chemical radiative collisions), then at moderate gas temperatures ($T\lesssim 0.1$ eV), the repulsive forces will not, in general, allow the atom A to reach a small enough distance that would correspond to a strong bond AB. The probability of events such as (3) in the gas mixture A + BC is then very small. However, there are important exceptions to this. They occur when the quasimolecule ABC has an ionic-type term. A particular feature of the ionic term is that it has a considerable depth, even at large distances between the colliding heavy particles at which repulsion corresponding to the covalent term is still negligible. The presence of the ionic term is associated with the existence of the so-called harpoon reactions which are known to proceed with large cross sections.[7,8] We shall now briefly explain the physics of harpoon reactions so that we can subsequently confine our attention to the analogous chemical radiative collisions.

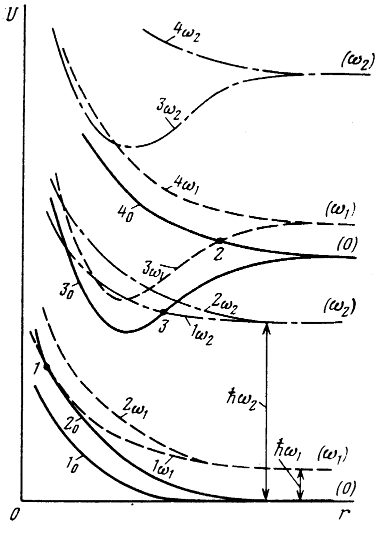

FIG. 1. Term values of the compound system A + B.

3. The classical harpoon reactions are usually taken to involve the substitution of an alkali-metal atom M for a halogen atom X in a molecule X_2:

$$M+X_2\rightarrow MX+X. \tag{4}$$

A necessary condition for this harpoon reaction is that the electron affinity of the molecule X_2 should be large enough and the ionization of the atom M relatively low. This requirement is connected with the following mechanism of the harpoon reaction. Suppose that the particles M and X_2 approach each other along the covalent term of the quasimolecule MX_2 until they reach $r(M, X_2)\approx r_0$, which corresponds to the quasicrossing point of the ionic and covalent terms, at which the charge transfer process

$$M+X_2\rightarrow M^++X_2^- \tag{5}$$

takes place. The molecular ion X_2^- is frequently in a loose state during this process and, as the particles M^+ and X_2^- move along the ionic term, the ion dissociates. When the charge transfer occurs on a sufficiently deep segment of the ionic term, the particles M^+ and X^- are found to be bonded together after the decay of X_2^-. This bonding can be broken, at least in principle, at the expense of the recoil energy in the case of transition to high vibrational states because of the large amount of kinetic energy taken up by M and X_2^- during the decay of X_2^-.

Harpoon reactions are possible if the crossing of the ionic and covalent terms occurs at large distances, $r_0 \gg 1$ a.u. ≈ 0.5 Å. Near $r(M, X_2) \approx r_0$, the terms are almost horizontal and the ionic term $M^+ + X_2^-$ is determined by the Coulomb interaction potential. The position of the crossing point can therefore be estimated from the formula

$$r_0 = (J_M - EA_{X_2})^{-1} \text{ a.u.}, \tag{6}$$

where J_M is the ionization energy of the atom M and EA_{X_2} is the so-called vertical electron affinity[1)] of the molecule X_2. The formula given by (6) is valid if the difference between J_M and EA_{X_2} is small in comparison with the characteristic atomic energy 1 a.u. ≈ 27 eV. In harpoon reactions, the difference $J_M - EA_X$ does not usually exceed 3 eV and, therefore, $r_0 \sim 10-30$ a.u.

In the case of a collision between a halogen molecule X_2 and an inert-gas atom R, the harpoon reaction will not, of course, occur. This is connected with the large ionization energy J_R of inert-gas atoms, as a result of which the ionic and ground covalent terms of the system RX_2 do not cross. In fact, exchange forces strongly distort the Coulomb shape of the ionic term prior to its crossing of the covalent term over distances $r(R, X_2) \sim (J_R - EA_{X_2})^{-1} \sim 1$ a.u. The excited atom R behaves similarly to an alkali-metal atom. The covalent term corresponding to the electronically excited state of the quasimolecule can then cross the ionic term, and the result of the harpoon reaction

$$R^* + X_2 \to (RX)^* + X \tag{7}$$

will be the molecule $(RX)^*$, which is excited not only vibrationally but also electronically.[9] Thus, by illuminating different atoms A with the resonance radiation, it is possible to force them into a violent chemical reaction with halogens.

4. Let us now consider the harpoon-type chemical RC reaction:

$$R + X_2 + \hbar\omega \rightleftharpoons R^+ + X_2^- \to (RX)^* + X. \tag{8}$$

The frequency ω of the monochromatic radiation will be assumed to be well removed from the frequencies of the characteristic emission of the atom R. It is clear that, instead of X_2, one can have another molecule with sufficiently high electron affinity (for example, NF_3, NO_2, or UF_6) and, instead of the inert-gas atom, we can have some other atom but, to be specific, we shall always refer to halogen molecules and inert-gas atoms.

As already noted, radiative collisions are characterized by transitions of the compound system at the crossing points of the terms (0) and (ω). As a rule, the number of such points is relatively large, but their contributions are very dependent on the experimental conditions. We shall again use the relatively simple picture shown in Fig. 1. We shall assume that it describes a gas consisting of atomic particles A = R and B = X_2. According to this figure, the crossing point 1 of the two lowest terms (0) and (ω) of the compound system $R + X_2 + \hbar\omega_1$ lies quite high and is the only one. This means that, at low temperatures ($T \ll \hbar\omega_1$), the $R + X_2$ gas is transparent to radiation of frequency ω_1. When the temperature is relatively high, one must take into account the presence of molecules with kinetic energies $\sim\hbar\omega_1$. Accordingly, the crossing point 1 of the terms 2_0 and 1_{ω_1} may become important. All this means that, as the temperature of the $R + X_2$ gas increases, the gas begins to absorb light of frequency ω_1. Electronic excitation of the gas molecule leads to a similar result. Thus, the presence of the crossing point 2 between the terms 3_{ω_1} and 4_0 may lead to absorption by the recombining $R + X_2$ plasma at relatively low gas temperatures. The disposition of the terms of the compound system $R + X_2 + \hbar\omega_2$ indicates that the cold excited gas will be opaque to light of the higher frequency ω_2. The reason for the absorption of light under these conditions must be sought in radiative collisions defined by the crossing point 3 between the terms 1_{ω_2} and 3_0. If the term 3_0 (in the present case, this is the ionic term $R^+ + X^-$) is sufficiently deep, the range of frequencies ω_2 for which radiative collisions take place may amount to a few hundred angstroms. The second stage of the radiative collision (8), i.e., the breakup of the molecular ion X_2^- with the formation of the bound state RX, should, in principle, proceed as in the ordinary harpoon reaction.

As already noted, transition to the ionic term is due to the light field which compensates the energy defect so that the terms of the compound system cross at relatively large distances

$$r_{\Delta\omega} = (J_R - EA_{X_2} - \hbar\omega)^{-1} \equiv (\Delta\omega)^{-1} \text{ a.u.} \tag{9}$$

In other words, the frequency of the radiation stimulating harpoon RC should be chosen so that the distance $r_{\Delta\omega}$ is of the order of the values for which ordinary harpoon reactions proceed at a high rate. We shall assume that, after transition to the ionic term, the second stage of the reaction (8) will take place with probability close to unity until the next crossing point is traversed. As already noted, other eventualities are possible, at least in principle, for example, the complete breakup of the complex $(RX_2)^*$ with the formation of three fragments: $R^* + X + X$. However, these situations will not be analyzed here because the assumptions made above are usually satisfied in the case of ordinary harpoon reactions. In view of the foregoing, the probability of the chemical RC under consideration after two crossing points have been traversed can be written by analogy with the Landau-Zener formula in the form

$$w = (1 - e^{-\delta_1}) + e^{\delta_1}(1 - e^{-\delta_2}). \tag{10}$$

Here, $\exp(-\delta_1)$, $\exp(-\delta_2)$ are the probabilities of remaining in the previous state after passing through the first and second crossing points, respectively; $\delta_{1,2} = 2\pi[V_{fi}(\theta_{1,2})]^2/(u_r \Delta F)$ is well-known nonadiabatic parameter, $V_{if}(\theta_k)$ is the matrix element of the transition $RX_2(i) \to RX_2(f)$, θ_1 and θ_2 are the angles between the light-field vector and the dipole moment of the system RX_2 at the first and second crossing points, respectively, u_r is the radial component of the relative velocity of the particles R and X_2, and ΔF is the modulus of the distance between the slopes of the ionic and covalent terms at their crossing point [$\Delta F \equiv (\Delta\omega)^2$ a.u.]. The formula given by (10) differs from the corresponding expressions for the radiative collisions of atoms and atomic ions by the absence of the factor $\exp(-\delta_2)$ from the first term. This is connected with the above assumption of dissociation prior to the second crossing point.

So far, for simplicity, we have confined our attention to the crossing of the ionic covalent terms. Actually, it is also necessary to take into account the motion of the nuclei of the molecule X_2 and the molecular ion X_2^-. This means that the transition matrix element must be evaluated not only with the wave functions of the electronic states corresponding to the covalent and ionic terms, but also with the radial wave functions of the molecule X_2 and the molecular ion X_2^- (r is the separation between the X nuclei). Thus, the nonadiabatic parameter can be written in the form

$$\delta_{1,2}=\delta_0(\cos\theta_{1,2})^2,\qquad \delta_0=\frac{2\pi d^2(\mathscr{E}_0)^2}{u_r(\Delta\omega)^2}Q. \tag{11}$$

where d is the matrix element of the dipole moment of the transition between the ionic and covalent terms, evaluated for electronic wave functions with the separation between R and X_2 equal to $r_{\Delta\omega}$, $\mathscr{E}_0$ is the amplitude of the monochromatic electromagnetic field producing the RC transition, and

$$Q=\int\limits_{\Delta E}\left|\int\chi_{X_2}(r')\chi_{X_2^-}(r')\,dr'\right|^2 dE \tag{12}$$

is a quantity analogous to the Franck-Condon factor, i.e., it is the square of the modulus of the overlap integral for the radial wave functions of X_2 and X_2^-, integrated over the energy band $\Delta E=(dU_{X_2^-}/dr)\Delta r$ corresponding to the dissociation of the ion X_2^- (Fig. 2).

To obtain the rate constant K for the radiative collision under investigation in a given light field, we must integrate the transition probability (10) with respect to the impact parameter ρ, then multiply by the relative velocity u, and finally average over the Maxwell distribution of the heavy particles at temperature T. The result of all this is the expression

$$K(r_{\Delta\omega},T,\alpha)=\int\limits_0^\infty d\varepsilon\frac{2}{\pi^{1/2}}T^{-3/2}e^{-\varepsilon/T}\varepsilon^{1/2}\int 2\pi\rho\,d\rho\langle w\rangle$$
$$=\int\limits_0^\infty d\varepsilon\frac{2}{\pi^{1/2}}T^{-3/2}e^{-\varepsilon/T}\varepsilon^{1/2}\int\limits_0^{r_{\Delta\omega}}d\rho\,2\pi\rho\left[1-\left\langle\exp\left(-\frac{\alpha}{(\varepsilon/T)^{1/2}}\frac{\cos^2\theta_1+\cos^2\theta_2}{[1-\rho^2/(r_{\Delta\omega})^2]^{1/2}}\right)\right\rangle\right] \tag{13}$$

where the angle brackets represent averaging over the angles θ_1 and θ_2, the parameter $\alpha=(\mathscr{E}_0/\mathscr{E}_c)^2$ is a measure of the strength of the electromagnetic field, $\mathscr{E}_c=u_T(\Delta\omega)^2/2\pi d^2Qr_{\Delta\omega}$ is the characteristic field strength at which the nonlinear dependence of the reaction rate on the light intensity sets in, $I\sim(\mathscr{E}_0)^2$ is the intensity, $u_T=(2T/\mu)^{1/2}$ is the relative thermal velocity, and μ is the reduced mass of the quasimolecules. In the expression for the radial velocity, $u_r=u[1-(\rho/r_{\Delta\omega})^2]^{1/2}$, we use the fact that repulsion on the covalent term is still unimportant for $r\approx r_{\Delta\omega}$. The evaluation of the integrals in (13) is simplified by the fact that the position of the crossing points is independent of the centrifugal energy. The result is of the form (cf. [6])

$$K(r_{\Delta\omega},T,\alpha)=K_c(r_{\Delta\omega})\overline{w}(\alpha), \tag{14}$$

where $K_c(r_{\Delta\omega})=2\pi^{1/2}(r_{\Delta\omega})^2u_T$ is the maximum possible rate constant of the chemical RC. This expression can be used in estimates of the rate constant of the usual harpoon reaction, where $\overline{w}(\alpha)$ is the average probability of the RC transition after passing through the two crossing points. It is given by

$$\overline{w}(\alpha)=2\int\limits_0^\infty dx\,xe^{-x^2}\left\{1-\left\langle\exp\left[-\frac{\alpha}{x}(\cos^2\theta_1+\cos^2\theta_2)\right]\right\rangle\right\}$$
$$=\begin{cases}(2\pi^{1/2}/3)\alpha & \alpha\ll1,\\ 1 & \alpha\gg1.\end{cases} \tag{15}$$

We note that, in contrast to the usual RC, the rate constant for the chemical RC does not fall in strong fields $\mathscr{E}_0\gg\mathscr{E}_c(\alpha\gg1)$, and ceases to depend on $\mathscr{E}_0$ because, in the scheme discussed above, the ion dissociates before it reaches the second crossing point.

It follows from (14) and (15) that, when low-intensity light is employed $[(\mathscr{E}_0)^2\ll(\mathscr{E}_c)^2]$, the rate constant for the chemical RC under consideration differs from the very high rate constants for the usual harpoon reactions by the small factor $\alpha\ll1$, whereas, for light of high intensity $[(\mathscr{E}_0)^2\gg(\mathscr{E}_c)^2]$, it is of the same order as these constants.

5. Following the work of Zhdanov and Chibisov,[10] it is possible to show that the asymptotic expression for the dipole moment of the transition[2)] is

$$d(r)=BC(n)r^{n-1}e^{-r/n}. \tag{16}$$

Here, $n=(1/2E_-)^{1/2}$ is the effective principal quantum number and E_- is the sum of the vertical electron affinity of the molecule X_2 and the inter-ion interaction potential at the point $r_{\Delta\omega}$, $B\approx1-5$ a.u. is a constant characterizing the behavior of the wave function of the outer electron of the negative ion,

$$C(n)\approx8\left[\frac{2}{n}(2l+1)\frac{l+m}{l-m}\right]^{1/2}\frac{(n/2)^m}{m!}\left(\frac{0{,}73}{n}\right)\left(\frac{n}{n+1}\right)^5\left(\frac{n-1}{n+1}\right)^{n-1}\Gamma(1-n), \tag{17}$$

l, m are the azimuthal and magnetic quantum numbers of the electron, and $\Gamma(x)$ is the gamma function.

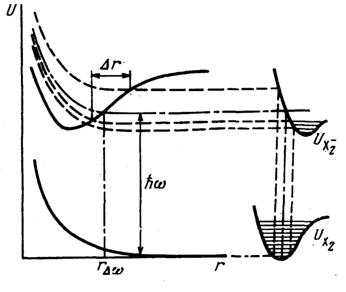

FIG. 2.

Let us now consider some numerical estimates for the harpoon chemical RC between a xenon atom and a halogen molecule. Let $u_T=5\times10^4$ cm·sec^{-1}, $EA_{X_2}=1.5$ eV,[11] $r_{\Delta\omega}=8$ a.u. ≈4 Å, $B=5$, $Q=1$, and $\hbar\omega=7.6$ eV. We then have $[d(r_{\Delta\omega})]^2\approx4\times10^{-2}$ a.u. For the limiting rate constants of the harpoon RC, we obtain $K_c(r_{\Delta\omega})\approx8\times10^{-2}$ a.u. $\approx4\times10^{-2}$ a.u. $\approx4\times10^{-10}$ cm^3·sec^{-1}, for which $(\mathscr{E}_c)^2\approx10^{-5}$ a.u., $\mathscr{E}_c\approx2\times10^7$ V/cm. Thus, cross sections of the order of the atomic cross sections (for which $K(r_{\Delta\omega}, T, \alpha) \sim 10^{-8}$ cm^3/sec) are reached in fields $\mathscr{E}_0 \approx 10^6$ V/cm. In the case of weak fields $[(\mathscr{E}_0)^2 \ll (\mathscr{E}_0)^2]$, the main characteristic of chemical RC is the absorption coefficient for the radiation, i.e., the radiation power absorbed per unit volume, divided by the energy flux density. The absorption coefficient for chemical RC can be written in the form

$$\varkappa(\Delta\omega, T) = q(\Delta\omega) N_R N_{X_2}. \tag{18}$$

where N_z is the gas concentration, $z = \mathrm{R}, \mathrm{X}_2$, and $q(\Delta\omega)$ is the reduced absorption coefficient (in the present case, the absorption coefficient per particle pair). Under these conditions,[6]

$$q(\Delta\omega) = K_c(r_{\Delta\omega}) \frac{16\pi}{3c(\mathscr{E}_c)^2}. \tag{19}$$

For the above parameter values, we obtain $q \sim 10^{-39}-10^{-38}$ cm^3. It follows that, for concentrations N_R, N_{X_2} such that $(N_R N_{X_2})^{1/2} \approx 1$ amagat $\approx 3\times10^{19}$ cm^{-3}, the absorption coefficient reaches $\varkappa \sim 1$ cm^{-1}.

6. We have carried out an experimental verification of the above theoretical predictions. The results of our experiments are briefly summarized below.

There are a number of ways in which chemical RC can be investigated experimentally. The most interesting are: a) studies of the absorption of the mixture $\mathrm{R} + \mathrm{X}_2$ at frequencies ω differing from the characteristic frequencies of the atom R and molecule X_2; b) studies of the radiation emitted by the molecules RX* obtained as a result of the chemical RC, and c) detection of the formation of the molecules RX or the products of their interaction with X_2. In the experiments on the detection of the effect of chemical RC, we have so far confined our attention to studies of the absorption spectra.

The absorption bands connected with chemical RC between atoms and halogen molecules lie in the following energy bands for the different inert gases:

He) 16–18 eV, Ne) 13–15 eV, Ar) 9.5–10.5 eV,

Kr) 7.5–8.5 eV, Xe) 6.5–7.5 eV.

Thus, for the first three gases, the bands correspond to the far ultraviolet, where measurements are quite difficult, whereas, for the last two gases, namely, krypton and xenon, one can use lithium fluoride windows so that the problem becomes much simpler.

In choosing between krypton and xenon, we prefer the latter because halogen mixtures always contain oxygen among their impurities and oxygen has its maximum absorption in the region between 7.5 and 8 eV.[12] Moreover, among the halogens, only fluorine is transparent in the band 6.5–7.5 eV. For the first experiments, we have, therefore, chosen the system $\mathrm{Xe} + \mathrm{F}_2$, despite the well-known difficulties connected with the toxicity and chemical activity of fluorine.

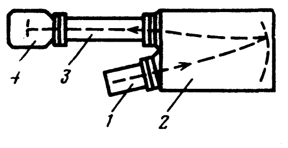

FIG. 3. Schematic illustration of the apparatus: 1—source of radiation (hydrogen lamp); 2—monochromator; 3—cell containing gas mixture (Xe, F_2, $\mathrm{Xe}+\mathrm{F}_2$); 4—photomultiplier.

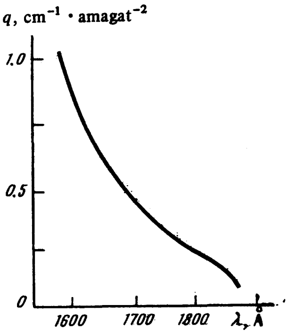

FIG. 4. Absorption coefficient corresponding to the chemical RC as a function of wavelength.

We measured the photomultiplier current produced by light transmitted by a cell filled with this gas mixture. The system is illustrated schematically in Fig. 3. The measurements were performed on: a) an evacuated cell, b) a cell filled with pure xenon, c) a cell filled with fluorine at pressures between 6 and 20 Torr, and d) a cell filled with a mixture of fluorine and xenon. The last mixture was produced by adding xenon to a cell containing fluorine after the spectrum of the latter was recorded. The spectra of the mixture $\mathrm{Xe} + \mathrm{F}_2$ were recorded 10 and 30 min after the xenon gas was introduced into the cell, both at room temperature and at −78 °C.

Figure 4 shows the measured absorption coefficient of the mixture

$$q = \frac{\ln(I_2/I_1)}{l C_{\mathrm{Xe}} C_{\mathrm{F}_2}} \tag{20}$$

as a function of the wavelength of the incident radiation, where I_1 and I_2 are the photomultiplier currents corresponding to pure fluorine and the mixture $\mathrm{Xe} + \mathrm{F}_2$, l is the length of the absorbing medium in centimeters, and C_{Xe} and C_{F_2} are concentrations of Xe and F_2 in amagat ($N_X \approx 3\times10^{19} C_X$). The measurements could not be carried out at wavelengths below 1580 Å because of the rapid fall in the intensity of the emission spectrum of the light source. Moreover, this region requires careful analysis because of the photoassociative absorption of light by xenon.[13] In the range 1580–1850 Å, on the other hand, absorption is due to the following chemical RC:

$$\mathrm{Xe} + \mathrm{F}_2 + \hbar\omega \rightarrow (\mathrm{XeF})^* + \mathrm{F}. \tag{21}$$

We have also analyzed other possible ways of explaining the observed absorption effect and have come to the conclusion that interpretations not based on chemical RC are in conflict with experimental results. This conclusion is supported by the following considerations.

One might try to interpret the observed absorption as being due to products of the reaction of either fluorine with xenon with the formation of xenon difluoride or fluorine with impurities contained in xenon. Reactions with the impurities can, in principle, result in, for example, HF, but these reactions can, in general, occur both in the dark and photochemically. This explanation is, however, in conflict with the following facts.

a) The absorption coefficient is approximately proportional to the product of the fluorine and xenon concentrations.

b) The observed absorption spectrum is very different from the spectrum of XeF_2[14] whereas absorption in HF should be much less than that observed under our conditions.[15]

c) No evidence was found for a strong temperature dependence of the intensity in the absorption spectrum or for the variation of the spectra with time.

d) The amount of fluorine in the cell did not change when xenon was admitted and remained constant in time.

e) Estimates of the amount and type of chemical products that could have been formed during the interaction between fluorine and impurities in the xenon lead to the conclusion that the observed absorption band cannot be ascribed to these products.

On the other hand, both the magnitude of the absorption coefficient and the frequency band predicted above on the basis of theoretical considerations (see also Dubov *et al.*[16]) for the chemical RC described by (21) are in good agreement with the results of measurements. There is thus every reason to suppose that the chemical RC effect has been theoretically predicted and experimentally verified.

7. Chemical RC is not merely an interesting effect: it is important from the practical point of view as well. It is likely that chemical RC can be used to maintain appreciable concentrations of unstable eximeric compounds and can produce chemical reactions in different systems with minimum expenditure of energy. Studies of the absorption spectra of chemical RC should provide information on the term structure of the corresponding eximeric molecules. It would also be interesting to examine the angular distribution of particles scattered during the chemical RC for different wavelengths of the radiation stimulating these reactions.

Morever, chemical RC of the type defined by (2) and (3), and more complicated RC, can, at least in principle, facilitate the production of compounds with lower expenditure of energy than in traditional methods such as the heating of a gas or plasma electrons (this includes plasma chemical methods, heating of vibrational degrees of freedom by laser radiation, and so on, all of which are under development at present). In other words, chemical RC can be used as an effective means of transforming light energy into chemical energy. Problems associated with this kind of chemical energy conversion are currently very topical. In particular, they are of considerable interest in connection with the expected substantial progress in the development of high-energy laser systems.[17]

As an illustration, let us consider the reaction given by (21). Suppose we have a source of light producing radiation of wavelength $\lambda < 1850$ A (frequencies $\approx \omega_0$). The chemical RC defined by (21) can be used to transform this energy into the energy of the excited molecules $(XeF)^*$. The corresponding ionic term of the molecule $(XeF)^*$ is then involved in population inversion relative to the lower covalent electronic states of XeF. Generation will then take place on the transition

$$(XeF)^* \begin{array}{l} \nearrow XeF + \hbar\omega_1 \\ \\ \searrow Xe + F + \hbar\omega_2 \end{array} \qquad (22)$$

for sufficiently high levels of pump power.[17] At the same time, XeF_2 is formed from the chemical products of (22) in a dense medium. It follows that the result of all these transitions is the conversion of light energy of frequency $\approx \omega_0$ into the energy of laser radiation at frequency $\omega \approx \omega_1, \omega_2$ and the chemical binding energy of XeF_2. The thermal losses in each event are then much less than $\hbar\omega_0$.

[1)] The vertical electron affinity EA_U is the difference between the ground-state energy of the molecule (U) and the corresponding part of the molecular-ion term U^- given by the Franck–Condon principle. We assume here that $EA_U > 0$ if the negative molecular-ion term lies below the molecular term.

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