Excitation processes in slow K^+–He, Ne, Ar, H_2, N_2 and Na^+–He collisions

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(Submitted 17 February 1984; resubmitted 29 June 1984)
Zh. Eksp. Teor. Fiz. **87**, 1906–1913 (December 1984)

Quasimolecular features of excitation processes in K^+–He, Ne, Ar, H_2, N_2 and Na^+–He collisions were investigated by measuring the cross sections for the emission of the resonance lines of potassium ($\lambda = 766.5$ and 769.9 nm), sodium ($\lambda = 589$ and 589.6 nm), and helium ($\lambda = 584$ nm) atoms at ion energies in the range 0.5–10 keV. In Na^+–He collisions, the resonance-line excitation functions obtained for sodium and helium atoms exhibit oscillations that are in antiphase and are due to phase interference between the quasimolecular states of the system of colliding particles. Experimental data on K^+–Ar collisions are interpreted in terms of schematic correlation diagrams for molecular orbitals. The excitation mechanisms for K^+–N_2 and K^+–Ar have been found to be similar, and this leads to the conclusion that the quasimolecular model used for the ion-atom case is also valid for the ion-molecule case. It is shown that the excitation of the $4p$-state of the potassium atom in the K^+–Ar case is due to a Landau-Zener type of interaction in the region of the quasicrossing of $(KAr)^+$ terms. Analysis of the excitation of this state in K^+–N_2 collisions also shows that the capture of an electron into the excited $4p$-state of the potassium atom is due to a nonadiabatic transition in the region of quasicrossing of energy terms of the same symmetry.

INTRODUCTION

Studies of excitation processes in slow ion-atom collisions yield extensive data on the quasimolecular mechanism of interaction between the colliding partners. In particular, quasimolecular features of the collision process can be seen in the regular oscillations of total excitation cross sections, which are interpreted in terms of phase interference between quasimolecular states,[1,2] (Rosenthal-Bobashev model).

Molecular terms of the system of colliding particles are used in the quantitative description of excitation processes in ion-atom collisions. At present, such terms have been calculated for only a small number of simple systems, so that schematic correlation diagrams for molecular orbitals are widely used but provide only a qualitative explanation of the known features of excitation processes. However, theoretical calculations alone are insufficient for complete understanding of the interaction picture because of the multichannel character of the processes under investigation. Our ideas on the collision mechanism must be founded on a wide class of experimental studies, including studies of inelastic energy loss spectra, the composition of the radiation, the spectra of the removed electrons, and so on. This comprehensive approach to ion-ion collisions has so far been carried out only for Na^+–Ne pairs.[3] The situation is still more complicated in the case of ion-molecule collsions. The interpretation of experimental data in the latter case demands a knowledge of the potential energy surfaces of the ion-molecule system. Calculations of such surfaces are so complicated that only a qualitative discussion of the experimental results is possible in many practical problems. It seems to us that a useful preliminary approach to the analysis of ion-molecule processes is to start by considering the analogy with ion-atom collisions. This approach is based on experimental data obtained in recent years, for example, for the He^+–N_2^+ pair,[4] which show that there are regular oscillations in th excitation cross sections for the 4^1D and 4^3D levels of the helium atom which are characteristic for ion-atom collisions. The Demkov model[6] has been used[5] for the H^+–N_2 case. It is suitable for ion-atom collisions and predicts the energy dependence of the cross section for the excitation of the molecular ion N_2^+ to the $B^2\Sigma_u^+$ state during charge transfer, and there is good agreement between these predictions and experiment. Dowek *et al.*[7] have pointed out that there is an analogy between the He^+–N_2, O_2 pairs and the ion-atom pair He^+–Ar, and have used this to develop a schematic picture for the energy terms of the ion-molecule system and hence a qualitative explanation of excitation and charge transfer data for collisions to different inelastic channels. Analysis of these data and of the results obtained in the present investigation can be used to identify those cases for which the analogy with ion-atom collisions can be used to interpret ion-molecule data. An important point in this connection is that the energy defects and the nature of the polarization interaction at large distances between the particles must be the same for the pairs to be compared. Moreover, the isotropic part of the ion-molecule interaction potential, which is a function of the separation between the ion and the center of mass of the molecule, must be much greater than the anisotropic part which depends on the orientation of the internuclear axis of the molecule. On this basis, it is useful to select the target in the form of homonuclear molecules for which this condition is known to be satisfied. The three-center problem then reduces to the two-center problem and this means that, instead of energy surfaces, we can use term curves for the system of colliding particles. Molecules with filled orbitals are then likened to inert-gas atoms.

In this paper, we report systematic studies of excitation in ion-atom and ion-molecule collisions in a broad range of collision energies (0.5–10 keV), using optical spectroscopy in

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the vacuum ultraviolet and visible ranges (50–800 nm). The aim was to establish the structural features of spectral-line excitation functions, which are due to phase interference between quasimolecular states of the system of colliding particles. Particular attention was devoted to a search, whenever possible, for analogies between the excitation mechanism for collisions between alkali-metal ions and inert-gas atoms and simple homonuclear molecules.

To implement this program, we have measured the excitation functions for the resonance lines of the potassium atoms ($\lambda = 766.5$ and 769.9 nm) in K^+–He, Ne, At, H_2, N_2 collisions, the sodium ($\lambda = 589.0$ and 589.6 nm) and helium ($\lambda = 584$ nm) atoms in Na^+–He collisions, and the line $\lambda = 389.8$ nm due to the K^+ ion in K^+–He collisions.

APPARATUS AND METHOD OF MEASUREMENT

The experimental setup that we have used is shown schematically in Fig. 1. The alkali-metal ion beam leaving the surface-ionization source 1 was first accelerated to a predetermined energy. It was then focused by the quadrupole lenses 2 and analyzed by the mass spectrometer 3. The emerging ions passed through the collimating slits 4 and finally entered the collision chamber 5 filled with the gas under investigation. The ion current was measured by the collector 6 and the radiation emitted as a result of the excitation of colliding particles was observed at 90° to the direction of the ion beam. The spectral analysis of this emission was accomplished by two monochromators. The monochromator 7 (MDR-2) was used in the visible range 250–800 nm. The linear polarization of the emission in the visible part of the spectrum was analyzed by the polaroid 8 and the mica quarter-wave phase plate 9 in front of the entrance slit of the monochromator. The phase plate was placed after the polarizer, was rigidly coupled to it, and used to cancel the polarizing effect of the monochromator. The emission was recorded by the photomultipler 10 (FÉU-79) with a cooled cathode and operated in the current mode. The spectroscopic analysis of the emission in the vacuum ultraviolet (50–250 nm) was performed with the Seya-Namioka vacuum monochromator 11, incorporating a toroidal diffraction grating. The radiation was recorded by the secondary-electron multiplier 12 (VÉU-2A), used under integrating or pulse-counting conditions. The outputs of the photomultiplier and the secondary-electron multiplier were recorded by the electrometers 14 (U5-9) and 15 (U1-7). The polarization of the radiation in the vacuum ultraviolet was not taken into account. The radiation spectra were recorded on the chart of the electronic potentiometer 13 (EPP-09).

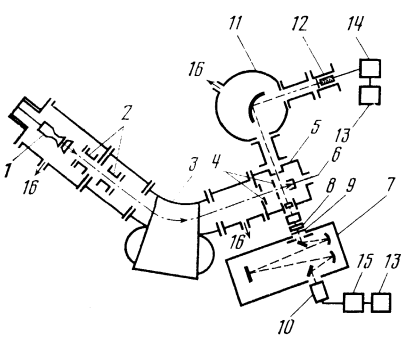

FIG. 1. Schematic diagram of apparatus.

The alkali-metal ion currents in the collision chamber were of the order of 0.1–1.0 μA and the pressure of the gas under investigation did not exceed 6×10^{-4} mm Hg, so that multiple collisions could be ignored. The system was pumped differentially by the oil-diffusion pump 16. The residual-gas pressure did no exceed 4×10^{-6} mm Hg.

The total cross section for the emission of a given spectral line was taken in the form

$$\sigma(\lambda)=C\frac{eS(\lambda)}{INLK(\lambda)}\left(1-\frac{P}{3}\right), \tag{1}$$

where C is a geometric factor that depends on the solid angle in which the monochromator collects radiation, I/e is the current of incident ions, N is the gas density in the target, L is the length of the light-collection region, $K(\lambda)$ is the spectral sensitivity of the light-recording system, and $S(\lambda)$ is the photomultiplier output signal. In our case, $S(\lambda)=S_{\parallel}(\lambda)+S_{\perp}(\lambda)$, where $S_{\parallel}(\lambda)$ and $S_{\perp}(\lambda)$ corresponds to radiation components with electric vectors respectively parallel and prependicular to the direction of the ion beam, and the degree of polarization is given by

$$P=[S_{\parallel}(\lambda)-S_{\perp}(\lambda)]/[S_{\parallel}(\lambda)+S_{\perp}(\lambda)]. \tag{2}$$

We measured the areas under the line profiles, which are proportional to $S_{\parallel}(\lambda)$ and $S_{\perp}(\lambda)$ the gas pressure, and the ion current. The absolute excitation cross sections for the resonance lines of potassium and sodium that were investigated in this research were determined by comparing the measured output signal with that due to the excitation of nitrogen by electron impact. Particular attention was therefore devoted to the reliable determination and control of the relative and absolute spectral sensitivity of the light-recording system in the visible part of the spectrum. This was done by measuring the photomultiplier output signal due to the (0, 1), (0, 2), (0,3), (0, 4), (1, 2), (1.3), and (1, 4) band in the first negative system of the ion N_2^+ ($B\,^2\Sigma_u^+ - X\,^2\Sigma_g^+$ transition) and the (4, 0), (4.1), (6, 2), (6, 3), (2, 0), (3, 0), (5, 1), and (5, 2) bands of the Meinel system ($A\,^2\Pi_u - X\,^2\Sigma_g^+$ transition) excited in collisions between the 110-eV electrons and nitrogen molecules. These bands cover the wavelength interval between 423.6 and 785.4 nm. The electron gun was located directly in front of the entrance slit of the collision chamber. The output signal was normalized to the (0, 1) band ($\lambda = 427.8$ nm) which had the highest intensity in this range. The relative spectral sensitivity curve of the recording system obtained in this way was compared with the relative excitation cross sections for the same bands, averaged over the experimental data reported in Refs. 8–13. The absolute excitation cross sections for the (0, 1) band ($\lambda = 427.8$ nm) was assumed to be 4.3×10^{-18} cm^2 at the electron energy of 110 eV. This figure was taken from Ref. 13.

The relative uncertainty in our measurements was 5%; the absolute uncertainty was 15%.

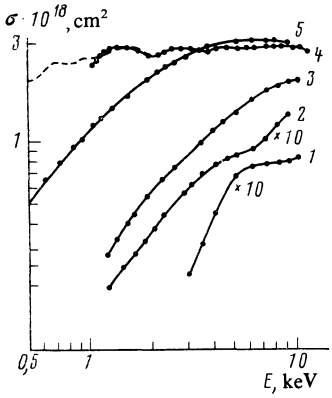

FIG. 2. Excitation function for the resonance line of the potassium atom ($\lambda = 766.5$ nm): 1—K^+–He; 2—K^+–Ne; 3—K^+–H_2; 4—K^+–Ar; 5—K^+–N_2. The dashed line represents the data given in Ref. 14 for K^+–Ar.

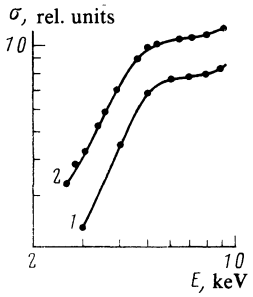

FIG. 3. Excitation functions for the line of the potassium atom ($\lambda = 766.5$ nm)—curve 1 and the K^+ ion ($\lambda = 389.5$ nm)—curve 2 in K^+–He collisions.

RESULTS OF MEASUREMENTS AND DISCUSSION

Figure 2 shows the data obtained in our study of the excitation function for the resonance line of the potassium atom ($\lambda = 766.5$ nm, $4pP_{3/2}$–$4sS_{1/2}$ transition) emitted in collisions between potassium ions and He, Ne, Ar atoms and H_2, N_2 molecules. It is clear from the figure that our data for the K^+–Ar pair agree to within experimental error with those reported in Ref. 14 (dashed line). The energy dependence of the excitation cross section in this energy range has a broad maximum and a weakly defined oscillatory structure. For K^+–N_2, the cross section reaches the maximum value at potassium-ion energies of 6–8 keV. This value is equal to the excitation cross section for the resonance line of the potassium atom in the case of the K^+–Ar pair. The excitation cross section for this particular line in the case of collisions between K^+ and He and Ne atoms at low energies is smaller by a factor of two, and at high energies by an order of magnitude, as compared with K^+–Ar, and the structural features are not observed. It follows from the results shown in Fig. 2 that the excitation cross section for the resonance line of the potassium atom in ion-atom collsions decreases as the energy defect ΔE increases from 13 eV for K^+–Ar to 21.8 eV for K^+–He. The reverse picture is observed for molecules. The excitation cross section for the resonance line of the potassium atom in K^+–N_2 collisions ($\Delta E = 12.9$ eV) is greater than for K^+–H_2 collisions ($\Delta E = 10.9$ eV).

To establish the mechanism responsible for the excitation of the $4p$ level of the potassium atom due to the multichannel character of the process under investigation, we must have not only the excitation function for the $4p$ level itself, but also the data on the total charge-transfer cross sections and the excitation cross sections corresponding to the individual inelastic channels.

Of the pairs that we have investigated, K^+–Ar has been studied most extensively. The total electron capture cross section was measured in Ref. 15. Comparison of our results with those reported in Ref. 15 shows that the contribution of the cross section for the capture of an electron to the $4p$ state of the potassium atom to the total charge-transfer cross section is small, so that the principal contribution is provided by capture to the $4s$ state. However, the energy dependence of these cross sections is the same: the cross sections reach their maxima at low K^+ energies ($E \sim 1$ keV) and vary slowly in a wide energy range.

The experimental results obtained for this pair can be explained qualitatively in terms of the schematic correlation diagrams for molecular orbitals.[16] Analysis of these diagrams shows that the capture to the ground $4s$ and excited $4p$ states of the potassium atom can occur as a result of transitions between terms of the same symmetry (Σ). The processes responsible for the population of these states are competing processes. The conclusion is supported by the fact that the terms corresponding to these states are populated from the same initial-state term. Moreover, the parameters of quasicrossing regions are such that the emission maxima occur for equal velocities. The substantial discrepancies between the magnitudes of the cross sections can probably be explained by the fact that the molecular terms of the system of colliding particles correspond to large internuclear distances R. The initial-state term first populates the term corresponding to the excitation of the $4s$ state and, after this, to the $4p$ state, at comparatively short distances R.

The foregoing leads to the conclusion that that excitation of the $4p$ state of potassium atom involves a Landau-Zener type of interaction in the region of quasicrossing of the Σ terms of the $K^+(3p^6)$–$Ar(3p^6)$ and $K(4p)$–$Ar(3p^5)$ states.

Apart from the resonance line of the potassium atom, we have also investigated the excitation of the K^+ ions and He atoms in K^+–He collisions. The results show that the helium atoms emit practically no radiation in the visible part of the spectrum for collision energies in the range $1 \leqslant E \leqslant 10$ keV. Figure 3 shows the excitation cross sections for the resonance line of the potassium atom and the $\lambda = 389.8$-nm line of the K^+ ion ($4p$–$4s$ transition) as functions of energy. The line due to the K^+ ion was recorded in second order of the diffraction grating, and absolute calibration was not performed. The data shown in the figure are therefore given in relative units. It is clear that the energy dependence of the excitation cross sections for these lines is similar. This suggests that there is a coupling between the inelastic channels leading to the population of the $4p$ state of the potassium ion and atom. On the other hand, one would expect the same energy dependence of the cross sections in the case of the excitation of the $3d$ level of the potassium atom and the $4p$ level of the ion K^+, since the terms corresponding to the

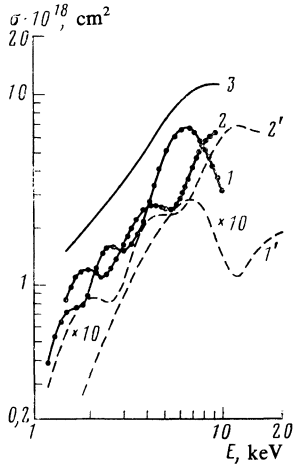

FIG. 4. Excitation functions for the resonance lines of the sodium and helium atoms in Na^+–He collisions: 1—NaI ($\lambda = 589$–589.6 nm); 2—HeI ($\lambda = 58.4$ nm); 3—total cross section for the excitation of the sodium and helium lines; 1′—NaI ($\lambda = 589$–589.6 nm)—taken from Ref. 17; 2′—HeI ($\lambda = 58.4$ nm)—taken from Ref. 18.

states K^+ $(4p)$–$He(1s^2)$ and $K(3d)$–$He^+(1s)$ are degenerate for large nuclear separations. Exchange interaction between these states may lead to the population of one of them through the other and, consequently, to the same energy dependence of the cross sections. It may therefore be considered that the excitation of the $4p$ level of the potassium atom is due to an appreciable contribution due to a cascade transition from the $3d$ to the $4p$ levels.

The oscillatory structure of the energy dependence of the excitation cross section is most clearly defined in Na^+–He collisions. Figure 4 shows the total excitation cross sections for the resonance line corresponding to the sodium doublet ($\lambda = 589$–589.6 nm, $3p$–$3s$ transition) and the resonance line of the helium atom ($\lambda = 58.4$ nm, $2p$–$1s$ transition). Comparison of our data with the results reported in Ref. 17 on the excitation of the sodium doublet, and in Ref. 18 on the excitation of the resonance line of the helium atom, shows that there is a considerable discrepancy between them. Moreover, the energy dependence of the excitation cross section for the sodium doublet is also very different (with the exception of the position of the peak at $E \simeq 6.5$ keV). We have observed an oscillatory structure which was not seen in Ref. 17. The energy dependence of the excitation cross section of the helium atom which we have found is the same as in Ref. 18, and the oscillations are in phase. The discrepancies as compared with Ref. 17 are due to the considerable experimental uncertainties introduced by the photographic method employed in Ref. 17 to record the radiation. This is also the explanation of the discrepancy between the magnitudes of the excitation cross sections for the resonance line of the helium atom, since the data from Ref. 17 were used in Ref. 18 to determine the absolute values of these cross sections.

Our results show that the oscillations on the excitation cross sections for the resonance lines of sodium and helium atoms are in antiphase. The excitation cross section for the resonance line of the helium atom (curve 2, Fig. 4) was determined by normalizing to the cross section for the excitation of this line Li^+–He collisions[19] at $E = 3$ keV. The curve obtained by summing the excitation cross sections for these lines turns out to be smooth over the entire energy range (curve 3). This means that the observed oscillations are, in fact, due to interference between the two quasimolecular states of the systems $Na^+(2p^6)$–$He(1s,2p)$ and $Na(2p^5 3p)$–$He^+(1s)$, and can be explained in terms of the Rosenthal-Bobashev model.

We note that the excitation of the individual lines of the doublet ($\lambda = 766.5$ and $\lambda = 769.9$ nm for potassium and $\lambda = 589$ and $\lambda = 589.6$ nm for sodium) was investigated both for K^+–Ar and Na^+–He. This showed that the ratio of the cross sections for these lines was close to two, which corresponds to the population of the states in accordance with their statistical weights. The cross sections for the components of the doublet then exhibit oscillation structures that are in phase.

Let us now consider the results on the excitation of the resonance line of the potassium atom in the ion-molecule collisions K^+–H_2, N_2. To identify the excitation mechanism, we shall use the results given in Ref. 20, where it is shown that, if capture of the electron occurs in a single inelastic channel as a result of interaction in a limited range of internuclear distances, the cross section for the process can be written in the form

$$\sigma(v) = K(v) \exp(-\alpha \Delta E / v), \tag{3}$$

where $K(v)$ is a slowly-varying function of the collision velocity v, ΔE is the energy defect of the inelastic process, and α is a constant. Figure 5 shows the excitation cross sections for the resonance line of the potassium atom on a semilogarithmic scale as a function of the reciprocal of the collision velocity $1/v$. It is clear that the logarithm of the cross section is a linear function of $1/v$, so that the excitation cross section for the $4p$ level of the potassium atom in K^+–H_2, N_2 collisions is satisfactorily described by (3). Hence, it may be concluded that the charge-transfer process leading to the excited $K(4p)$ state occurs in a restricted range of internuclear distances in a single inelastic channel. If this were not so, and other channels were involved, E would change and $\ln \sigma$ would not be a linear function of $1/v$.

In view of the foregoing, we may suppose that the capture of an electron to the $4p$ state of the potassium atom in

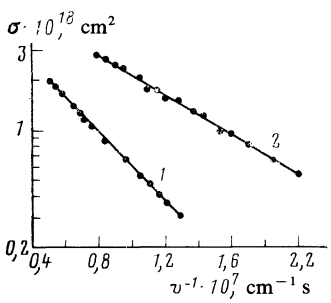

FIG. 5. Excitation functions for the resonance line of the potassium atom ($\lambda = 766.5$ nm) plotted against the reciprocal of the velocity of the K^+ ions: 1—K^+–H_2; 2—K^+–N_2.

K^+–H_2, N_2 collisions in the above energy range may be interpreted in the two-level approximation as the result of a nonadiabatic interaction in the region of the quasicrossing of the energy terms of the system of colliding particles.

To describe more concretely the mechanism responsible for excitation in the case of K^+–N_2 collisions, it is useful to consider the analogy with the ion-atom pair K^+–Ar. The justification for this is that the excitation of the K($4p$) state can be described in the two-level approximation in both cases. Moreover, the energy defects ($\Delta E \simeq 13$ eV) and the character of the polarization interaction at large internuclear separations R are the same. The excitation cross sections for the resonance line of the potassium atom for these pairs reach their maximum value for relatively low velocities of the K^+ ions. The maximum cross sections are close to each other, so that it may be considered that, by analogy with K^+–Ar, the excitation of the $4p$ state of the potassium atom in K^+–N_2 collisions is due to a nonadiabatic transition to the region of quasicrossing of energy terms of the same symmetry, which correspond to the states $K^+(3p^6)$–$N_2(X\,^1\Sigma_g^+)$ and $(4p)$–$N_2^+(X\,^2\Sigma_g^+)$.

The authors are indebted to Professor V. V. Afrosimov and S. V. Bobashev for interest in this research and for useful suggestions in the course of discussions.

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Translated by S. Chomet