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Fig. 1

Figure 1: Fig. 1

Abstract

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FEATURES OF THE SCATTERING OF FAST BEAMS OF O AND N ATOMS BY NO AND CO MOLECULES

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Usually, in describing a chemical transformation it is assumed that it is determined only by the relative configuration of the nuclei in the field caused by the interaction of the molecules. In doing so, one restricts oneself to reactions for which there are no transitions between electronic states in the course of the collision. Electronic transitions, which are quite probable when potential-energy surfaces intersect, may substantially affect the course of a chemical reaction. An exact calculation of potential-energy surfaces is an extraordinarily difficult problem; therefore the possibility of experimentally determining the energies at which intersections and the corresponding electronic transitions occur appears very attractive.

In work (^{1}) the possibility of carrying out such measurements was noted. In the present work, the investigation of elastic scattering of O and N atoms by CO and NO molecules was carried out on an apparatus similar to that used in (^{1}). Beams of N and O atoms were obtained by dissociative ionization of N_2 and CO_2 molecules and subsequent charge exchange of O^+ and N^+ in Kr and N_2, respectively. The choice of charge-exchange partners made it possible to obtain atoms in the ground electronic states $O(^3P)$ and $N(^4S)$.

Fig. 1

The determination of the parameters of an effective spherically symmetric repulsive potential of the form $V(r) = K/r^n$ is carried out by the usual procedure from the dependence of the scattering cross section Q on the beam energy E, as described in work (^{2}).

In Fig. 1, on a double logarithmic scale, the experimental dependences $\lg Q$ on $\lg E$ are presented (scattering curves); the dashed line shows the extrapolation of the initial linear portions. As follows from Fig. 1, only for the system N—NO can the parameters K and n be determined over the entire range of measured cross sections; for the remaining systems these parameters were determined from the initial linear portions.

The obtained values of K and n are summarized in Table 1, which also contains the intervals of distances over which these values are valid. The data of Table 1 are needed for calculating the transport coefficients of mixtures containing these components in the temperature range from 1000 to 10 000°K.

Of considerable interest are the sharp deviations from linearity found in the dependences of $\lg Q$ on $\lg E$ (Fig. 1).

One might try to explain the break in the scattering curve by the inadequacy of approximating the potential by a function $V = K/r^n$. However, even when the scattering curve is treated on the basis of an exponential potential (by the method of (^{3})), the feature in the form of a break is preserved. Since for all the systems studied (except N—CO) stable molecular states are known, another explanation of the observed breaks might be associated with the scattering of part of the beam in the effective field of repulsive forces, and part in the field of attraction. However, such an explanation apparently must be rejected for the following reasons.

Table 1

Parameters K and n of the potentials of the systems studied

System	K, eV · Å^n	n	Δr, Å
O—NO	801	9.00	2.41—1.89
N—NO	379	8.12	2.38—1.84
O—CO	761	9.30	2.33—1.80
N—CO	120	6.82	2.25—1.80

First, the steric factor corresponding to the formation of configurations of stable molecules is evidently very small, and this should strongly suppress the possible contribution of the attractive branch (in the same direction acts the allowance for the statistical weight of the electronic state of the bound state).

Furthermore, the difference between the internuclear distances of the scattering molecules (practically unchanged during the collision) and the corresponding distances in stable triatomic molecules is extremely unfavorable for the formation of bound states (thus, r_e(C—O) = 1.125 Å, whereas for CO_2 in a bent configuration r_e(C—O) = 1.246 Å).

Finally, an indication of another reason for the appearance of the observed breaks is provided by the results of work (^{1}) for the O—O_2 system. The scattering curve for this system is not at all similar to the curves in Fig. 1, although "binding" of O and O_2 into an ozone molecule undoubtedly took place.

In view of the foregoing, it may be assumed that the breaks in the dependences $Q(E)$ found in the present work are due to a sharp change in the interaction associated with the crossing of potential-energy surfaces. In the spherically symmetric approximation this corresponds to the crossing of potential curves, and thus the initial linear portion of Fig. 1 (continued by a dashed line) corresponds to an effective spherically symmetric repulsive potential, whose parameters are given in Table 1. It is called effective because it corresponds to all possible configurations of the atoms in the collision process. At the point of the break, a portion of the O atoms begins to interact with CO (or NO) according to a different law; the scattering of the main part of the atoms can still be described by the straight line (the dashed line in Fig. 1). Then the difference between the experimental values and the values corresponding to the dashed continuation characterizes the relative fraction of atoms for which a change in the nature of the interaction has occurred. The cause of such a change may be the crossing of the effective repulsive term of the O–CO system and the term of the bound state of the CO_2 molecule. At such a crossing, as a result of a nonadiabatic electronic transition, some of the atoms that up to this point had passed along the repulsive potential surfaces fall onto an attractive surface and therefore are scattered differently. This circumstance may lead to a break in the scattering curve, and the sharpness of the break apparently confirms the proposed explanation.

For the O—NO system, the complete similarity of the features of the scattering curve indicates the possibility of an analogous crossing of terms and an electronic transition for some of the atoms during scattering. An alternative explanation may be associated with the exchange reaction $O + NO \rightarrow N + O_2$, whose energy defect is quite close to the value of the interaction energy at the kink point.

The results obtained in the present work may make it possible to refine somewhat our information on the actual form of the potential-energy surfaces of the systems studied.

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