SHORT-RANGE FORCES OF THE INTERMOLECULAR INTERACTION OF OXYGEN AND NITROGEN

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Abstract

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The study of elastic scattering of nitrogen and oxygen molecules in their own gas and by atoms of noble gases is of great interest for the following reasons.

First, on the basis of the study of such systems it becomes possible to determine directly the effective spherically symmetric potentials of intermolecular interaction for oxygen and nitrogen, which are needed for calculating the kinetic properties of air at temperatures above 1000°K. A parallel study of the scattering of molecules by atoms of noble gases makes it possible to check an indirect method for determining the same potentials (^1). This indirect method will be useful when it is impossible to create targets from molecular gases.

Second, comparison of the potential curves with those obtained from data on the study of vibrational relaxation of molecules in a gas (^2) may make it possible to establish the degree of adequacy of the existing theories of vibrational relaxation.

Finally, the study of such systems makes it possible to obtain an estimate of the accuracy of the very useful semiempirical method for determining potential curves proposed by Mason, Vanderslice, and others (^3, ^4). This method, despite its wide use, suffers from uncertainty in the accuracy of the values of interaction potential energies predicted on its basis.

In the present work, the values of the parameters of the potential function of intermolecular interaction of the form $V(r) = K/r^s$ were found from the dependence on the energy of the total effective scattering cross section of a beam of fast ($E = 0.6$–4 keV) neutral nitrogen and oxygen molecules in oxygen, nitrogen, and argon. A description of the principle of the method and of the experimental apparatus is given in (^5). The relation connecting the effective scattering cross section $S(\theta_0, E)$ with the energy E, in the case $V = K/r^s$, has the form:

$$S(\theta_0, E) = \pi \left(\frac{KC(s)}{E\theta_0} \right)^{2/s}, \tag{1}$$

where θ_0 is the aperture angle; $C(s)$ is a numerical factor depending on s. With the aid of this relation, from the experimental dependence of S on E it is easy to find the parameters K and s, i.e., to reconstruct the potential function.

This relation was obtained for the case of a spherically symmetric force field. The systems under study do not possess spherical symmetry, which creates difficulties for determining the parameters of the potential from the experimental dependence of the effective cross section on energy.

Since, in scattering of a beam, effective averaging of cross sections depending on orientation takes place, one may try to choose a spherically symmetric potential of the form $V = K/r^s$ that describes the observed scattering pattern. If the dependence of the measured cross sections on energy is described by relation (1), then it is easy to find the corresponding values of the parameters K and S of the effective spherically symmetric potential. The parameters thus found are given in Table 1, where the intervals of distances of closest approach are also given, for which constancy of the values of K and s can be guaranteed.

In another approach, the force field of a homonuclear molecule can be represented either in the form of an orientation-dependent sum of two contributions corresponding to the individual atoms, or in the form of a one-center orientation-dependent potential. However, in the first case the relation between the experimentally measured cross section and the potential parameters loses its simple form, and the selection of the corresponding parameter values becomes accessible only to machine calculation. For heteronuclear molecules, experiments on elastic scattering cannot at present give potential parameters corresponding to the atomic contributions, since the number of unknown parameters is equal to 4. In the second case, a new parameter appears—the asphericity parameter—which likewise cannot be determined from the dependence of S on E.

Table 1

Parameters of the potentials of the investigated systems

System	K	s	Δr, Å
$N_2 - N_2$	550	7.4	2.34-3.05
$N_2 - Ar$*	1050	8.15	2.12-2.67
$N_2 - O_2$	330	6.8	2.34-3.05
$O_2 - O_2$	240	6.3	2.34-3.15
$O_2 - Ar$*	5000	9.9	2.15-2.63

* The results for $N_2 - Ar$ and $O_2 - Ar$, reported in the article by Yu. N. Belyaev and V. B. Leonas, ZhTF, **36**, 353 (1966), are erroneous. In the present work, refined values of the parameters K and s for these systems are given.

Comparison of the potential curves obtained in this work with those obtained in work (2) on the basis of data on relaxation of molecular vibrations in a

Fig. 1. Potential curves of the $O_2 - O_2$ system. 1 –according to the present work; 2 –according to work (4); 3 –according to (3).

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gas reveals poor agreement. The difference is mainly reduced to the greater steepness of the potential curves obtained from relaxation data. The currently existing theories of vibrational relaxation are not perfect, and therefore the errors in determining the potential curve include not only experimental errors but also errors of the theory. It may be assumed that the discrepancies found indicate the inadequacy of the theory of vibrational relaxation used in work (2).

Comparison of the experimental data with calculations based on the semiempirical method (3) revealed good agreement for nitrogen and considerably worse agreement for $O_2 - O_2$, $N_2 - O_2$. As is seen from Fig. 1, the potential curve of the $O_2 - O_2$ system obtained in work (3) is steeper than that obtained in the present work, and it may be stated that the refinements of the method made in work (4) lead to a significant improvement in the agreement of the data for the $O_2 - O_2$, $N_2 - O_2$ systems with experiment. It is of interest to check the fulfillment of the combination rule for intermolecular potentials. Combining the potential parameters of the $O_2 - O_2$ and $N_2 - N_2$ systems leads to values of the parameters of the $N_2 - O_2$ system that practically coincide with the experimental values.

Fig. 1. Potential curves of the $O_2 - O_2$ system. 1 –according to the present work; 2 –according to work (4); 3 –according to (3).

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