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ANISOTROPY OF INTERACTION IN SIMPLE SYSTEMS

F. VECCHIOCATIVI

University of Perugia
Dept. of Chemistry
Perugia, Italy

Anisotropy of Interaction in Simple Systems

Some considerations about the experimental techniques available for the study of scattering properties sensitive to the anisotropy of interaction in atom–atom and atom–diatom systems are reported. The theoretical approximations commonly used for obtaining information about the interaction potential from these experimental results are briefly discussed. Potential energy functions obtained by a combined analysis of different experimental observables with respect to those obtained by analyzing one property only are proven to be more reliable.

1. INTRODUCTION

It is customary to classify the interaction forces between atoms or molecules in two classes: the usual chemical bonds, and the weak, or van der Waals, forces which dominate when chemical bonds do not occur. While the anisotropy of chemical interactions determines the structures of a molecule and therefore, also, a large part of the chemical properties of the matter, the anisotropy of weak interactions is relevant to dynamical properties. Actually the anisotropy of intermolecular forces strongly affects several features of energy transfer processes which can occur in molecular collisions.

Obviously the interaction between two closed shell atoms is weak and isotropic, whereas the interaction between two open shell atoms very likely leads to the formation of a chemical bond. How-

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ever, when a closed shell atom interacts with an open shell atom not in an S-state, the anisotropy of the electron charge distribution of the latter leads to weak anisotropic interatomic interaction.

The atom–diatom interaction is always anisotropic, even when both partners are closed shells. However, it must be noted that when one of the two partners is an open shell, an additional complication in the anisotropy can occur. In fact when the open shell partner is an atom not in an S-state or a diatom not in a Σ-state, anisotropy of the type mentioned above for atom–atom systems is also present.

An important feature of atom–atom and atom–diatom systems showing a weak and anisotropic interaction is the presence of a level structure of that separated partner which is responsible for the anisotropy. For example, considering the $O(^3P)$–rare gas systems, at large interatomic separation, three J levels of the oxygen atom are possible. Moreover, considering the $N_2(^1\Sigma)$–rare gas atom systems at large separation, the rotational level structure of N_2 is present. When the two partners are approaching each other, because of this level structure and the anisotropy of interaction, several adiabatic pathways of the system are possible and during a collision nonadiabatic transitions could also occur.

In this Comment some techniques are summarized which have recently been used to obtain experimental scattering data for atom–atom and atom–diatom systems showing anisotropic weak interactions. Then the methods used to obtain accurate information from the analysis of these data about the anisotropy of interaction in these simple systems will be discussed.

2. SCATTERING EXPERIMENTS

The usefulness of molecular beam scattering experiments in obtaining detailed information about interatomic and intermolecular forces is well established. The possible interference structures which can be observed in the cross sections are a very sensitive probe of the potential energy function which describes the interaction between the two collision partners. When in these experiments an analysis of the states involved in the collision is also accomplished, the potential anisotropy can be well characterized. In this section recent experiments in this direction are summarized. It must be noted that only a sample of representative cases are reported here and not an exhaustive catalogue of the investigated systems.

2.A. Atom–Atom Systems

In scattering experiments without state selection the presence of an anisotropy of the atom–atom interaction can produce modifications in the interference structures when compared with those expected for isotropic interatomic forces. These irregularities have been observed in several atom–atom systems, both for the glory structure in the velocity dependence of the integral cross sections[1] and for the rainbow structure in the differential cross sections.[2,3] These experimental results clearly show the anisotropic nature of the interaction of several atom–atom systems. However, to obtain the details of the interaction anisotropy scattering experiments with state selection are necessary.

If the atom under study has to be in an excited state one possibility is to prepare this atom in a well-defined level by an appropriate laser frequency just before the collision. This has been done, for instance, for alkali atoms in the excited ^2P_J state colliding with rare gas atoms.[4,5] In some cases the excited atoms are obtained by a nonselective method and the atomic beam is then purified by quenching the undesired states with appropriate photons. This technique has been applied, for instance, in scattering experiments of metastable neon atoms[6]: a beam of Ne^* ($^3P_{2,0}$) is produced in a neon discharge or by electron bombardment of a neon beam; then laser light is used in order to quench selectively one of the two J states.

When the atom under study is a ground state atom a selective preparation or quenching by photons cannot be used. However in these cases a magnetic analysis of the m_J states has been successfully applied.[7] With this technique an inhomogeneous magnetic field is used to deflect the atoms from the beam direction according to their m_J value. Using this technique cross sections for oxygen,[8] fluorine[9] and gallium[10] atoms m_J-selected have been measured.

2.B. Atom–Diatom Systems

The anisotropy of the atom–atom interaction can also produce irregularities in the interference structures of the cross sections when measured without selection or analysis of the rotational states of the diatom. Actually, the damping of the glory undulations in the velocity dependence of the integral cross section and the quenching of the rainbow structure in the angular dependence of the differential cross section for atom–diatom collisions are well-known effects.[11] An influence of the diatom rotational temperature on the quenching of the glory undulations has also been experimentally observed.[12] In this case the oscillatory structure appears to be partially damped for collisions involving diatoms at low rotational temperature, as expected for an anisotropic interaction, but when the rotational temperature is increased the oscillation amplitude is undamped and the cross sections can be easily described using a phenomenological isotropic potential.

The case of NO–rare gas interactions deserves special mention. These systems have been extensively studied in several laboratories. The reason is that the NO molecule is in a $^2\Pi$-state. Consequently its rotational level structure together with the 3/2–1/2 splitting makes the anisotropy more complicated than for closed shell molecules.[13] Very interesting scattering experiments were performed a few years ago with oriented NO molecules by using appropriate electrical and magnetic fields.[14] These experiments have provided the anisotropy of the integral cross sections as a function of the collision velocity.

More detailed information about the angular dependence of the potential in the range probed by the collisions can be provided by experimental state-to-state rotationally inelastic cross sections. Accurate cross sections for processes of translational to rotational energy transfer have been measured essentially by two different methods: in crossed beam experiments the energy loss after the collision is obtained by the time-of-flight technique, whereas in the other method laser-induced fluorescence is used for the analysis of the rotational level population before and after the collision. With the latter method cross sections for rotational transitions of Na_2 in collisions with rare gas atoms have been measured.[15] The time-of-flight experiments have provided results on several other systems involving, for instance, H_2 and its isotopes,[16] N_2, O_2, and CO.[17]

3. ANALYSIS OF SCATTERING DATA

The most usual way to obtain information on the interaction potential and its anisotropy from scattering data is a best fit procedure. Here one has to consider that the effective potential to be used for cross section calculation can be considered as the sum of three contributions: (i) the electrostatic interaction with its anisotropy; (ii) the term which contains the centrifugal interaction due to the collisional angular momentum; (iii) the spin-orbit interaction in the atom–atom cases or the diatom rotational interaction in the atom–diatom cases. Therefore the calculation of all the observables implies the solution of the relevant coupled equations. This procedure could be accomplished by numerical routines but usually it takes such a long time that obtaining the interaction potential by data fitting could be rather hard. However, for each case suitable approximations can be used.

3.A. Analysis of Atom–Atom Results

For the analysis of atom–atom cross sections an adiabatic state approximation[7,18] is commonly used. As a function of the internuclear distance several possible states are defined. These states can be designated using the five Hund's cases. When these states are adiabatically connected, potential energy curves are obtained which correlate with the J-levels of the separated atomic partners. Cross sections can now be easily computed for each adiabatic curve and the experimental data can be compared with an appropriate combination of these cross sections. This combination takes into account the J-level population before the collision and possible nonadiabatic effects.

With the above procedure several systems have been studied, e.g., the F–rare gas systems. Differential[2] and integral[9] cross sections for these systems have been measured without state selection. Integral cross sections with magnetic analysis of the *m*-states are also available.[7,9] It has been shown that for thermal energy collisions nonadiabatic effects in these cases can be neglected. The analysis of all the scattering data together with the spectroscopic results have provided very accurate potential energy curves for the three $|J,\Omega\rangle$ adiabatic states of F–Xe [9]: the $|3/2,1/2\rangle$, $|3/2,3/2\rangle$ and $|1/2,1/2\rangle$ states which correlate, respectively, with the $^2\Sigma_{1/2}$, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states.

For F–Ar and F–Kr systems a complete data analysis is in progress,[19] the preliminary results showing some aspects of general interest. For the F–Ar ground state the potential well falls completely in the region of the Hund case (c), where the good quantum number is Ω; for the F–Xe ground state in the potential well region the Hund case (a) is appropriate and therefore the good quantum number is Λ. This should be an indication of an almost chemical interaction for F–Xe in the ground state. Actually the equilibrium distance of 2.31 Å with a "bond" energy of 151.0 meV seems to corroborate this statement. On the other side the F–Ar ground state interaction appears to be a very weak interaction of the van der Waals type. In this case the equilibrium distance is at 3.25 Å with a potential well depth of 8.7 meV. For the F–Kr ground state interaction an intermediate situation occurs. This trend is also due to an increase of the anisotropy of the electrostatic interaction going from F–Ar to F–Xe.

3.B. Analysis of Atom–Diatom Results

Several approximations have been proposed for the description of atom–diatom collisions.[20] The effective potential can be simplified, keeping the rotational interaction constant by assuming a fixed value of the j rotational quantum number of the diatom. This is usually called the "energy sudden" approximation. Another possibility is keeping the centrifugal contribution constant by assuming a fixed value of the l quantum number of the collisional angular momentum. This is usually called the "centrifugal sudden" approximation. A third possibility is to assume fixed values for both j and l quantum numbers. This is the so-called "infinite order sudden" approximation. By analogy with the atom–atom cases an adiabatic state approximation has been very recently proposed, also, for atom–diatom collisions.[21] In this approximation the collision is assumed to be evolving along an adiabatic potential curve which correlates with a j rotational level of the separated diatom. The adiabatic cross sections are then combined taking into account the j level population before the collision and the nonadiabatic effects. Although this approximation has not yet been applied for the analysis of experimental data, preliminary results indicate that because of its accuracy and simplicity it could be very promising for future studies.

In several cases the infinite order sudden approximation has been applied for fitting integral, total differential or rotationally inelastic cross sections. Actually in some of these cases this approximation appears to be rather reliable. Close coupling calculations have been compared with the infinite order sudden approximation results using the same potential energy surface.[22] These results indicate that the agreement is satisfactory.

The potential energy surface for atom–diatom interaction is sometimes obtained in two steps: first, the spherical average of the interaction is obtained from those data not sensitive to the anisotropy; then the angular dependence of the potential is obtained from the other data.[23] For instance, the scattering data measured with a high rotational temperature can be assumed to be mainly sensitive to the spherical average of the potential energy surface.[12] In fact, when the diatoms are predominantly in relatively high rotational levels, many rotational cycles occur during the collision time and the cross sections are mainly determined by the spherical average interactions. Moreover, increasing the rotational energy, the transitions from one level to another become less probable because of the larger energy spacing. This explains, for instance, the dependence of the glory structure on the rotational temperature observed experimentally.[12,23]

Once the spherical average of the potential energy surface has been obtained, the anisotropy can be assessed from the analysis of the integral and total differential cross sections at a low rotational temperature and from the inelastic cross sections.[24]

4. CONCLUSIONS

Scattering data provide very detailed information about the interaction potential and its anisotropy. However, it must be stressed that different experiments (integral, total, differential, elastic or inelastic cross section measurements) or the same experiment performed under different conditions (e.g., the rotational temperature in atom–diatom collisions) can probe different characteristics of the potential energy function. Therefore, a potential obtained from the analysis of only one experiment shows a rather limited range of reliability. To extend this range a combined analysis of several

different observables from scattering experiments, but also from gaseous properties and, if available, from spectroscopic results, is necessary. The potential energy surface obtained by this multi-property analysis unifies all the experimental information in one single function. With such a procedure anisotropic interactions have been determined for some atom–atom and atom–diatom systems.[9,23,25] In our opinion this is the right way for obtaining potential energy functions of a reliability matching the level of accuracy of the experimental data available today.

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FRANCO VECCHIOCATTIVI
Dipartimento di Chimica,
Universitá di Perugia,
06100 Perugia, Italy

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