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Dissociative attachment in CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4

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by

Shi-Chung Chu

A DISSERTATION

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Dissociative Attachment in

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Advisor: Paul D. Burrow

This dissertation presents an electron beam study of the dissociative attachment process in the chloromethanes. A novel design of a high sensitivity ion counting system was incorporated in this work.

Each chloromethane displays two peaks in the dissociative attachment cross section below an electron energy of 1 eV, with the first peak consistently at zero energy and the second peak ranging from 0.27 to 0.80 eV. A systematic increase of the dissociative attachment cross sections is observed each time a Cl atom replaces an H atom. The ratio of the cross sections near zero electron energy between the highest and lowest attachers, namely CCl_4 and CH_3Cl respectively, is approximately six orders of magnitude, consistent with the earlier swarm measurements.

Also included in this dissertation is the application of the dissociative attachment process to study gas-surface vibrational energy exchange. In this work, cool gas was allowed to flow through a heated tube and then intercepted by the electron beam at right angles. N_2O was used in this study because its dissociative attachment cross section is very sensitive to temperature, permiting us to use it as a diagnostic tool for the measurement of vibrational temperature.

TITLE

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BY

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To my parents

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Chapter 1

Introduction

This dissertation deals with one particular type of electron-molecule interaction, namely the dissociative attachment (also referred to as DA hereafter) process. The first part of this work describes measurements of the DA cross section in a family of related molecules, i.e., the chloromethanes. Low energy electron impact on the chloromethanes has been studied experimentally by a number of authors (Scheunemann et al., 1980; Schultes et al., 1975 and references therein), but considerable disagreements about the magnitudes and shapes of the cross sections exist in the existing literature. To resolve these questions, more careful measurements in the chloromethanes are indispensable, which is the motivation of this work. The second part deals with the application of dissociative attachment in N_2O as a diagnostic tool in the study of the accommodation of vibrationally excited molecules on hot surfaces. The latter work was, in fact, carried out first and the requirement for improved detection sensitivity became the stimulus for the modified apparatus which is described in the first part of the work.

To give an outline of this dissertation, it begins with a general review of DA and the experimental methods to measure the DA cross sections in Chapter 2. Then in Chapter 3, the design and construction of the apparatus, i.e., the high sensitivity ion counting system, used in the present study to measure the cross sections of the chloromethanes are described. The performance of this ion counting system is evaluated in Chapter 4. Finally, in Chapter 5, the measured total DA cross sections of the chloromethanes are presented and discussed. An independent subject, the study of vibrationally excited N_2O on hot surfaces is discussed in Chapter 6. A little more detailed description of the contents in each chapter will be given later in this chapter.

Let us now examine the DA process which yields a neutral atomic or molecular fragment along with a stable negative ion upon electron impact as shown in Equation 1.1.

$$e^- + XY \rightarrow X^- + Y. \tag{1.1}$$

It can occur, therefore, only in molecules whose fragments have positive electron affinities. This process can be understood by first forming a temporary negative ion state

$$e^- + XY \rightarrow XY^{-*} \rightarrow X^- + Y, \tag{1.2}$$

where e^- is the incident electron, XY is the target molecule and XY^{-*} is a temporary negative ion. Briefly, the incident electron is first captured by the target molecule to form a temporary negative ion, it then dissociates into an anion fragment and neutral fragment(s) if it survives the

autodetaching process. Thus, the magnitude of a DA cross section can be conveniently expressed as the capture cross section of the incident electron by the target molecule times a survival probability for dissociation.

In Chapter 2, these concepts are reviewed briefly along with the classifications of temporary anions. Shape and core-excited resonances, which play an important role in DA processes, are discussed. Temperature and isotope effects, which affect the magnitudes of DA cross sections, are also discussed. In addition to the DA process, ion pair formation, which proceeds without an intermediate temporary negative ion state, was also observed in the chloromethane molecules. Thus, a brief introduction regarding this process is also given. Finally, the experimental techniques used to study the DA process, primarily the electron beam and electron swarm methods, are described.

In Chapter 3, the high sensitivity ion counting system, designed for studying small signals is described. It begins with a discussion of the trochoidal electron monochromator which produces the monoenergetic electron beam. The electron beam is crossed by a molecular beam at right angles in the collision region. The collision region design is the result of several conflicting requirements, since we want to collect as many of the fragment ions as possible, which requires high draw-out voltages, and high energy resolution of the electron beam is still desired. The transport of negative ions from the collision region to the detector, a multi-channel plate (MCP) electron multiplier, is next discussed. Finally, the hardware and software that control the experiments are discussed.

The characteristics of the present ion counting system are described in Chapter 4. Knowledge of the system performance is important in determining the absolute total DA cross sections of the molecules under study. In particular, the role of discrimination against ions of different kinetic energies is examined by comparing with previously studied benchmark molecular systems such as CO_2. The shielding properties of the present grid design in the collision region are studied along with the field dependence of the electron energy resolution. The linearity of the anion yield as a function of source chamber pressure and electron beam current are shown. The collection efficiency of the anion yield in the present counting system was found to be a function of the B-field and tests were carried out to determine the influence of this effect on our measurements.

The results of the total dissociative attachment cross section measurements in the chloromethanes are given in Chapter 5. Each molecule exhibits a sharp peak near zero electron energy and a relatively broad peak below 1 eV. The DA cross section increases rapidly when an H atom is replaced by a Cl atom, yielding a cross section ratio of more than 6 orders of magnitude between the zero energy peaks of CCl_4 and CH_3Cl.

The motivation for the high sensitivity apparatus was provided by a study in which we attempted to use the DA process as a diagnostic means to determine the vibrational temperature of a gas (N_2O) emerging from a tubular oven. Although this work was not brought to an entirely satisfactory conclusion, we have demonstrated that the concept is workable. A new study using the high sensitivity apparatus will be the subject for the

next generation of graduate student. The details of our preliminary work are discussed in Chapter 6. In short, the vibrational temperature of N_2O emerging from a tubular oven was found to be lower than the temperature of the oven, suggesting that vibrational thermal equilibrium condition has not been reached. With the high sensitivity apparatus, one expects to see the approach of the vibrational temperature of N_2O towards thermal equilibrium as N_2O molecules make *more* wall collisions within the tubular oven, in other words, as the length to diameter ratio of the oven is increased.

In Appendix A, a general equation used to calculate the potential around the collision region with grids that surround the electron beam is derived. A simplified model that simulates the design of the collision region is used in deriving this equation, hence the results are only approximate. Nevertheless, it gives us some insight about the potential distribution. The model used for deriving this equation incorporated equally spaced infinitely long line charges at equal distances which are parallel to the axis of an infinitely long cylindrical electrode. The line image charge method and superposition principle are used in the derivation. The variation of the potential for different numbers of line charges, the line charge location and different sizes of the line charge obtained by use of this equation are shown in Appendix A.

In Appendix B, a program written in the BASIC computer language which controls the counting experiment is listed. This program is written in such a way that the parameters such as the electron impact energy range, electron impact energy increment and the counting time interval for