Forschung, Wissenschaft

Electron Scattering Experiments: Gas Phase Reactions Involving Free Electrons *

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Abstract

The electron scattering field and its implications for both basic scientific knowledge and practical applications are briefly introduced. A preliminary account of a new experiment within this field, a crossed beam study of the O^-/diatomic molecule reaction is then given. It was found that the studied molecules fall into two distinct classes with respect to associative electron detachment. In the first class, represented by O^-/CO and O^-/H_2 the liberated bond energy is transferred almost exclusively into the vibrational motion of the product molecule. In contrast, in the O^-/NO system a large fraction of the energy is given to the departing free electron.

The events which occur during the collision of a free electron with an isolated molecule in the gas phase have received much attention in the past 20 years. This renaissance of the electron scattering field has been initiated by the discovery by *George J. Schulz* in the 1960's of short-lived negative ions, also called resonances [1], as intermediate species in such collisions. The history and implications of this discovery have been described after the premature death of G. J. Schulz by scientists who actively participated in this research [2].

The importance of these resonances lies mainly in the fact that they increase the probability of energy transfer during the electron-molecule collision. The lifetime of such a transient negative ion or resonance, although at first sight esoterically short (mostly in the 10^{-11} - 10^{-15}s range) is still much longer than the time it takes a free electron with a few eV energy simply to pass a molecule without forming an intermediate complex. During this increased interaction time the probability of an energy transfer is much higher than in a simple collision. A dramatic example is the excitation of vibrational motion in a molecule by the impact of a few eV electron such as found for example in discharges. Before the discovery of resonances this probability was expected to be extremely small, based on the argument that the very light electron will not be able to set the heavy nuclei into motion, in much the same manner as a fly hitting an elephant will not set it into motion. It was not until the discovery of resonances that this expectation was shown to be drastically wrong. The resonance causes very efficient vibrational excitation because the intermediate negative ion has a different equilibrium internuclear separation and the different potential which prevails during its lifetime sets the nuclei into motion. The resonant vibrational excitation was found to be several orders of magnitude larger than the "direct" excitation. This phenomenon is of the utmost importance for example in the discharge of the CO_2 laser, where in the initial step the kinetic energy of an electron is converted into vibrational excitation of a N_2 molecule.

To measure and theoretically understand these electron scattering phenomena has been a challenge to both experimentalists and theoreticians and the observed phenomena represent a beautiful demonstration of the laws of quantum mechanics. As an example the vibrational excitation in N_2 by electron impact can be mentioned, where the intermediate N_2^- shows a surprising "pseudovibrational" structure where the "vibrational" levels shift depending upon the channel of observation. This phenomenon has eluded explanation for some time and has then been rationalised by Herzenberg by the so called boomerang model [3]:

This model is applicable to cases where the lifetime of the negative ion is comparable to the vibrational period of the molecule (that is around 10^{-14} s) such as the lowest N_2^- state. During this very short lifetime the nuclei do not have enough time to complete several vibrations and the usual definite vibrational levels literally do not have enough time to develop. Instead, after the formation of N_2^-, which has a longer equilibrium internuclear separation than N_2 itself, the nuclei start to move apart, are then turned back at the outer slope of the potential curve and return (boomerang motion). This motion will be carried out only once since at this point the N_2^- decays by electron detachment. The observed structure is then the result of interference of the outgoing and reflected nuclear waves. Thanks to the very short duration of the negative ion state a dynamic picture of moving nuclei appears from this experiment, instead of the usual stationary picture of

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fixed vibrational levels which is obtained in experiments concerned with longer time scales (as for example infrared spectroscopy).

The knowledge of the properties of the resonances also turned out to be of great practical interest. They are often of dominant importance whenever free electrons and molecules are present. Thus the applications range from astrochemistry over laser plasmas to the design of magnetohydrodynamic generators [4]. Resonances have also been proposed as intermediates in ozone synthesis [4], an important commercial chemical production [5].

The results of these research activities have so far mostly been described in physics journals and were concerned with atoms and small molecules. However, the techniques which have been developed are finding increasing application in chemistry. Thus electron transmission spectrocopy, which measures negative electron affinities, has been used as a probe for the "experimental" unoccupied orbital energies [6]. Electron energy loss spectroscopy has been used to determine the energies of triplets and other normaly inaccessible states of molecules which are of importance in photochemistry [7]. The applications of these two techniques in chemistry are presently exploited in Fribourg [8, 9].

A major limitation of the conventional experiments described above where free electrons are collided with molecules is that the processes observed are "vertical", the observations being confined to the Franck-Condon region. The possibility to overcome this limitation and learn something about the processes far from the equilibrium nuclear configurations of the neutral ground state molecule was the strongest incentive for the original research which has been carried out at Yale University and is concerned with electron detachment in the collisions of a stable atomic negative ion with atoms and diatomic molecules and observing the process by means of the ejected electrons. The following section gives a preliminary account of the associative electron detachment in collisions of O^- with CO, H_2 and NO. Full description of the experiments and the apparatus developed for this study will be published later [10].

Associative electron detachment is an ion-molecule reaction of the form.

$$O^- + M \rightarrow MO + e^- + E$$

where M is a diatomic molecule and MO is a product triatomic molecule. The excess energy E is equal to the liberated bond energy minus the electron affinity of the oxygen atom (1.46 eV) and is partitioned between the vibrational-rotational modes of the product molecule and the kinetic energy of the outgoing electron. In this study we concentrate on very low incident O^- kinetic energies where associative detachment is the only energetically allowed process leading to electron detachment. Collisional detachment

$$O^- + M \rightarrow M + O + e^-$$

where the kinetic energy of the incident O^- is used to overcome the electron affinity of the oxygen atom, becomes energetically allowed for incident O^- energies larger than 1.46 eV.

We studied the detachment process in a crossed beam apparatus where an O^- beam of variable energy is crossed with an effusive gas beam. The detached electrons are collected at a variable angle respective to the O^- beam, energy analysed and counted.

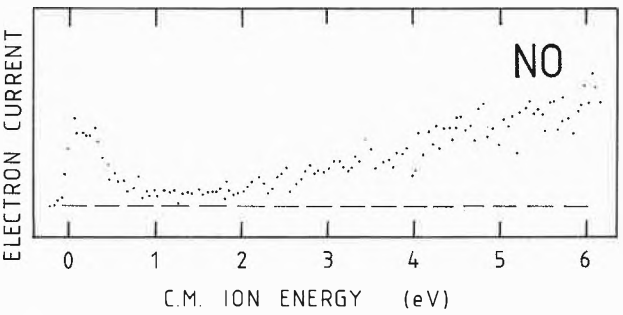

Fig. 1: Dependence of the detached electron signal in O^-/NO collisions on the O^- center of mass kinetic energy. Angle of observation is 90°.

Fig. 1 shows the yield of the detached electrons as a function of the O^- kinetic energy. A large cross section is observed in the associative detachment region below 1 eV, followed by a minimum and then a gradual rise above 1.46 eV where collisional detachment also becomes energetically allowed. This observation is consistent with the picture obtained previously by *Comer* and *Schulz* [11] from total detachment cross sections in O^-/H_2, O^-/CO and O^-/N_2. The behaviour seems to be general for all molecules which form stable compounds with the oxygen atom and where associative detachment is energetically possible (class 2 in the classification scheme of ref. [11]).

To characterize the reaction in the interesting associative detachment region, 0–1 eV, knowledge of the final (vibrational) state distribution of the product triatomic molecule is required. We obtained this information from the measured kinetic energies of the ejected electrons.

All three ion molecule reactions are strongly exothermic and the present experiment gives information about the partition of the available energy between the internal vibrational-rotational modes of the product triatomic molecule and the kinetic energy of the outgoing electron. The detached electron spectra are compared in Fig. 2. The spectra were recorded with O^- center-of-mass energies of 0.2, 0.1, and 0.3 eV for CO, H_2 and NO, respectively, and were found to vary little within the O^- energy range 0.1–0.5 eV. They are thus representative of very low O^- energies.

In CO and H_2 the electrons concentrate at low energies, 0–0.3 eV, much less than the corresponding reaction exothermicities of 4 eV and 3.5 eV. In contrast, a broad

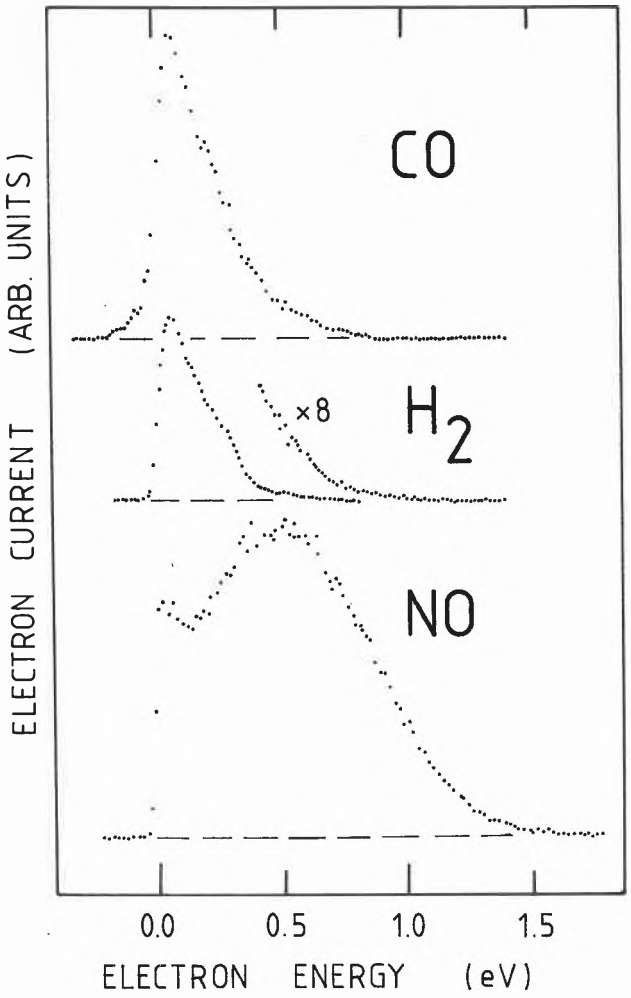

Fig. 2: Energy spectra of the detached electrons in collisions of O^- with diatomic molecules, observed at 90°. The spectra are not corrected for variations in instrument transmission with energy.

energy distribution is observed in the O^-/NO system, extending up to the allowed limit of 1.65 eV given by the reaction exothermicity for zero energy O^- ions. Thus, in the case of CO and H_2, virtually all the reaction exothermicity appears as internal vibrational-rotational excitation of the product molecule, whereas in the case of NO a significant fraction of the available energy is transferred to the outgoing electron.

It may be seen that we encounter two distinctly different types of behaviour among these systems. In the first class including the O^-/CO and O^-/H_2 systems essentially all the available energy is left as vibrational-rotational excitation of the product. In the second class, represented by the O^-/NO system, low lying vibrational-rotational states of the product NO_2 are also populated with significant probability and a large fraction of the available energy is transferred to the outgoing electron. The absence of vibrational structure indicates that all vibrational and many rotational states are populated to a certain degree without pronounced selection. These observations should be important for further development of the active field of collisional detachment theory and will have bearing on the physics of the upper atmosphere. The last system, O^-/NO represents a phenomenologically interesting case, where chemical energy of the O–NO bond is not degraded as heat as one might expect, but appears as the kinetic energy of a free electron. It could be called, therefore, a "chemical" source of free electrons.

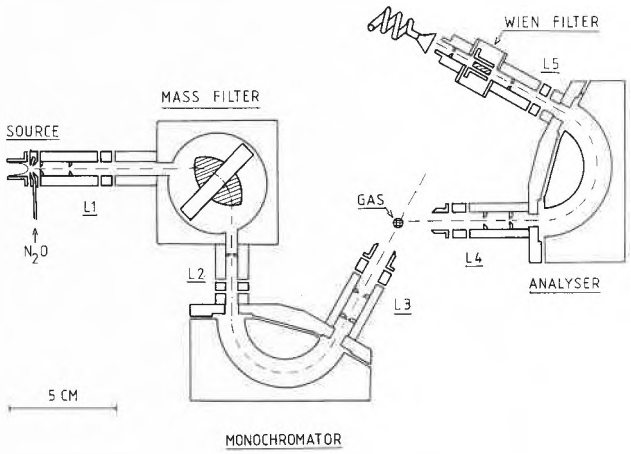

Fig. 3: Diagram of the electron/ion impact spectrometer developed for the electron detachment experiments. L1–L5 are electrostatic lenses.

By far the greatest effort involved in these experiments so far has been invested in the construction of the apparatus. Its details will be published later [10] and only a brief description is given here. The diagram is given in Fig. 3. It is a crossed beam type instrument where an energy and mass selected beam of O^- ions crosses an effusive gas beam from a nozzle. The detached electrons are collected at a variable angle, energy and mass analyzed and counted. The O^- ions are formed in dissociative attachment in N_2O at the surface of a hot thoria coated iridium filament, traverse a magnetic sector mass filter and a 150° spherical condenser-type electrostatic energy selector. The scattered particles are energy analyzed by another 150° spherical condenser-type energy selector, electron or ion detection is selected by a Wien-type analyzer and the particles are finally counted with a channel electron multiplier. The instrument allows switching from O^- beam to electron beam by merely changing the solenoid current of the magnetic sector mass analyzer and keeping all other conditions constant. Thus, for calibration purposes, electron scattering in He was used. The energy scale of the detector was calibrated on the sharp features $1^1S \rightarrow 2^3S$ threshold excitation by electron impact in He. The experimental parameter requiring particular attention in the present experiment is the uniformity of detector transmission over the very large dynamic range of energies between near zero and 1.7 eV. The transmission

curve has been determined by the standard technique using the uniform ionization continuum near threshold in He. The curve obtained with the present instrument has a deviation of the signal from a constant of the order of $\pm$ 20% and the onset of electron detection is around 0.05 eV. The most serious imperfection is the rapid variation of the transmission around 0.2 eV. The similar structure around 0.2 eV in the O^-, NO spectrum in Fig. 1 might be entirely due to this nonuniformity in detector transmission.

The particular requirements of the experiment necessitate the use of special materials. Thus all electron and ion optics are made of molybdenum, known to have very uniform surface potentials. Most structural parts are made of titanium, in order to avoid the weak magnetism often associated with stainless steel.

In conclusion, low energy, high resolution electron scattering experiments have brought a large amount of information of both fundamental scientific interest and practical importance. The experimental methods developed in this field are likely to find increasing applications in chemistry in the future.

The construction of the ion collision apparatus and the electron detachment experiments were carried out at Yale University and I would like to express my thanks to Prof. S. F. Wong for his support during this work.

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