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EXPERIMENTAL CHEMICAL KINETICS

A STUDY OF CHEMICAL REACTIONS BY MEANS OF MOLECULAR BEAM TECHNIQUES

Progress Report

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ABSTRACT

Beams of electrons are shown to be able to control the motions of neutral molecules. A beam of electrons coaxial with a neutral beam of KCl molecules can restrict the divergence of the KCl beam to increase its signal on a detector by up to a factor of 10^4. Further an electron beam can pump molecules from the residual gas in a vacuum chamber by forcing them to move preferentially along the electron beam into another chamber where they are detected by a mass spectrometer.

Inelastic scattering of CsI by Ar and Xe and of CsCl by Ar with velocity selection and analysis at thermal energies shows large cross sections for the transfer of energy in amounts up to several vibrational quanta for both excitation and deexcitation of the molecules.

The reaction LiCl + H $\longrightarrow$ Li + HCl is studied as it occurs on a Re surface as are the yields of positive and negative ions formed from cesium halides incident on a Nb surface.

The progress made on work supported by ERDA Contract No. AT(11-1)-3129 since October 1974 is as follows:

1. Publications

   a. S.M. Bobbio, C.T. Chiou, E.F. Greene, and H.D. Lambropoulos. Reduction of the angular divergence of a molecular beam by a coaxial beam of electrons. J. Chem. Phys., 62, 190 (1975). Reprints are enclosed.

   b. N.A. Sondergaard and E.A. Mason. Delta function model for interatomic forces: correlation scheme for closed shell atoms and ions. J. Chem. Phys., 62, 1299 (1975). Reprints are enclosed.

   c. E.F. Greene, R.B. Hall, and E.A. Mason. Vanishing rainbows near orbiting and the energy dependence of rainbow scattering: relation to properties of the potential. J. Chem. Phys., 62, 3554 (1975). Reprints are enclosed.

   d. W.D. Armstrong, R.J. Conley, R.P. Creaser, E.F. Greene, and R.B. Hall. The elastic and inelastic scattering of diatomic molecules by atoms: CsI + Ar, CsCl + Ar, CsI + Xe. J. Chem. Phys., 63, 000 (1975). Preprints are enclosed.

2. Status of current research

   The progress made on the several projects being studied is as follows:

   a. The inelastic scattering of alkali halides by rare gases. The first part of the work (See Section 1d) will be published shortly. This deals with measurements for which the detector for the halide moves in a plane perpendicular to the beam of rare gas. Several runs have now been made with the detector moving in the plane of the two beams. This permits measurements near the centroid which can show the presence of ballistic scattering, a surprising result observed at Harvard (H.J. Loesch and D.R. Herschbach, J. Chem. Phys., 57, 2038 (1972)) for the same kinds of system at higher energies. Ballistic scattering occurs when a large fraction of the energy of relative motion is transferred to internal energy of the colliding particles as a result of the collision. Our recent work has suffered from having a low signal-to-noise ratio for some reason not as yet clear. However, up to now we find no evidence of large amounts of ballistic scattering.

A counting system built recently is now ready to permit digital recording of the scattered signals, but as yet other sources of noise have remained too large to permit use of the counting circuits. Several steps are being taken to reduce the noise, and better measurements are expected to be possible soon.

Another part of this project has been measurement of the velocity distribution of CsI vapor coming from the source. The shape of this distribution gives evidence of how much the internal energy of the CsI is reduced during the expansion of the jet from the source. We believe that both rotational and vibrational energy are efficiently transferred to the energy of directed flow of the molecules. Typically CsI at 1200 K in the source appears to have internal temperatures for vibration and rotation of about 800 K after the expansion.

b. The control of the motion of neutral molecules by a beam of electrons.

Our first results on this study are described in the work cited (1a). In further work we have found that an electronic beam in a vacuum chamber can deliver molecules from the residual gas through a hole or slit into a second chamber containing a mass spectrometer. Some results (Fig.1) show the increase in total pressure recorded by an EAI Quad 150A mass spectrometer* as this pressure varies when an electronic beam in an adjoining chamber is rotated by an angle θ. By definition the electronic beam, the connecting slit and the ion source of the spectrometer are aligned for $\theta = 0$. This result seems to show that the electronic beam is a directional pump for neutral molecules which enter the beam at random but leave preferentially along its direction. Perhaps the effect can be used to increase the sensitivity of mass spectrometers to gases at low pressures. The signal at mass 28, presumably N_2 or CO, is proportional to the total pressure. However the signal at mass 32, presumably O_2, is decreased to 10% or less of its normal value when the electron beam is on. This indicates that the "O_2" may be made more reactive by being raised to an activated state which is then removed to form oxidation products on collisions with molecules of pump oil or the walls of the chamber. The removal of mass 32 is less for $\theta = 0$ than for other angles which shows some collimation of the "O_2" remaining.

In other studies of the interaction of molecular and electronic beams we have used two velocity selectors, selector 1 and selector 2, in series to see if the interaction of the electrons with a selected beam produces any change in speed of the molecules.

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* The mass spectrometer has been kindly loaned to us by Professor P. Estrup.

Fig. 2 gives some results. The unselected distribution from the source measured using selector 2 shows not only an increase in intensity but a considerable apparent "acceleration" when the electronic beam is used (I_N) compared to when the electrons are absent (I_p). However, when the distribution from the source is first narrowed by passing through selector 1 the "acceleration" is greatly reduced while the increased intensity remains. This is consistent with our model for the effect which attributes the "acceleration" to a velocity dependent filter effect. The larger scattering cross section for slower molecules in the beam makes their attenuation greater than that for faster molecules. This support for the model suggests that it may be used with increased confidence in understanding the nature of the force between the electronic beam and the neutral molecules.

A modified configuraton in which an electrostatic lens precedes the collimation of the electronic by the coaxial solenoid produces considerable further increases in the efficiency with which the molecules are collected. The detected signal of KCl neutrals with the electrons present for collimation can be 10^4 times as great as with the electrons absent. Experiments are being set up to measure the distribution of the electron beam throughout its path.

c. The use of measurements of rainbow scattering to learn about the potential. The theoretical part of the work has been published (Section 1c). We would have liked to carry out experimental measurements of the rainbow angle as it varied with energy near the transition to orbiting. Unfortunately, the experimental accuracy we have available now does not make an experiment seem likely to succeed. It has been postponed for the present.

d. The reaction of atoms and molecules on surfaces. Dr. R.B. Hall has done a preliminary study of the reaction LiCl + H $\longrightarrow$ Li + HCl on a Re surface in the temperature range 1000-1400K. The first results seem to show a need to return to simpler experiments to establish the behavior of LiCl and Li separately on Re. The system seems worth further study, as an example of a simple reaction taking place in two dimensions, but there are no clear cut results yet. Mass analysis of the particles leaving the surface may be necessary.

e. Formation of positive and negative ions from cesium halides on Nb surfaces. Several years ago (Progress Report, October, 1973; COO-3129-35) we measured the efficiencies β_+ and β_- with which Cs^+ and I^- ions were formed from beams of CsI hitting a hot Nb surface. The variation of β with the temperature of the surface seemed consistent with a quasi-equilibrium model for the ionization (the usual Saha-Langmuir model) and promised to give information about

the dissociation energy of NbI by use of a simple extension of the model (A.Persky, E.F. Greene, and A. Kuppermann, J. Chem. Phys., 49, 2347 (1968)). Recently we have measured $\beta_-(T)$ for halide ions formed from all the Cs halides. The predictions of the equilibrium model seem to be born out in a general way, but the precision of the results was poor. More careful design of the experiments with such improvements as mass analysis for the ions seems to be needed.

3. Personnel

Several people have worked on projects supported by the contract during the past year. The numbers in parentheses after the names refer to the sections of this report in which each one's work is described.

Dr. R.B. Hall (1c, 1d, 2a, 2d) is compleing his third year as a research associate. He will leave in October to join the Exxon Research Laboratory.

Professor R.N. Nelson (2e) of Georgia Southern College was a research associate for 2 months in the summer of 1975.

Mr. N.A. Sondergaard (1b, 2a) is a graduate student who has finished his 4th year of graduate work. He should complete work for his Ph.D. by June 1976.

Mr. H.D. Lambropoulos (1a, 2b) is in his 4th year of graduate work. He should finish work for his Ph.D. within a year.

Mr. W. Holber (2b) is an undergraduate majoring in physics. His work will represent his senior thesis.

Collaboration with Professor E.A. Mason (1b, 1c) has continued to be profitable to the members of the group.

Professor E.F. Greene, the principal investigator, has spent 50% of his time on work supported by the contract since the start of the current term. No change is expected in this fraction for the rest of the term.

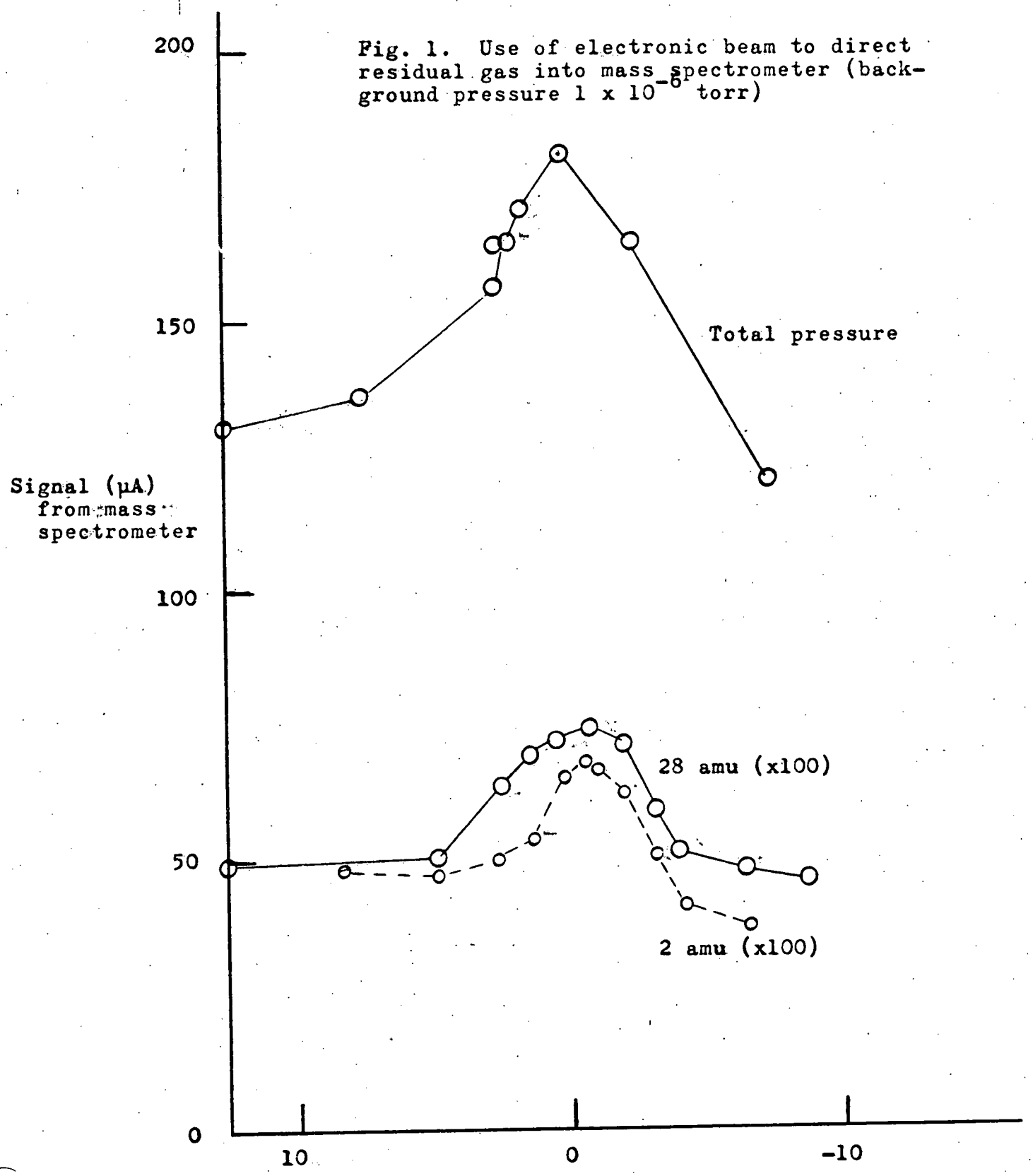

Fig. 1. Use of electronic beam to direct residual gas into mass spectrometer (background pressure 1 x 10^{-6} torr)

Fig. 2. Flux of beam of KCl to detector in presence (I_N) and absence (I_p) of coaxial beam of electrons