Threshold behavior of endothermic reactions: $C^+(^2P) + H_2 \rightarrow CH^+ + H$

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The reaction

$$C^+(^2P) + H_2 \rightarrow CH^+ + H \qquad (1)$$

and its deuterium analog is a model system in ion–molecule chemistry. It is of interest due to its astrophysical significance, because it is an endothermic process, and because the interaction involves several potential energy surfaces. Experimental work has included determinations of the total reaction cross section,[1-3] studies of the reaction dynamics,[4] measurements of product internal energy distributions,[5] and chemiluminescence studies of electronically excited products.[6] Theoretical studies encompass *ab initio* potential energy surface computations,[7] classical trajectory studies,[8] and

phase space[9] and transition state[10] theory calculations.

Despite this attention, the total reaction cross section is not well characterized, especially near threshold. In this Communication, we present cross section measurements for reaction (1) obtained on a new apparatus designed to allow precise examination of ion–molecule reactions as a function of translational energy.

The on beam apparatus and data reduction procedures used in this work are described in detail elsewhere.[11] C^+ ions are produced by electron impact ionization of CO. By keeping the electron energy less than 25 eV, C^+ is produced exclusively in the ^2P ground state,[4(c)] presumably with a 2:1 statistical population of the $J = 3/2$ and $J = 1/2$ levels.

Mass analyzed C^+ ions with well-defined translational energies are allowed to react with H_2 in a gas cell. Unreacted C^+ ions and CH^+ product ions undergo mass analysis and are detected using standard ion counting techniques. The problem of secondary ion collection losses, which is common in conventional beam-gas experiments, is essentially eliminated by the use of the ion beam guide technique of Teloy and Gerlich.[12] This technique also permits low ion kinetic energies (<0.1 eV) and provides routine energy analysis. The absolute magnitudes of the cross sections reported here have an uncertainty of ± 20%.[11]

Figure 1 shows our results for the excitation function of reaction (1). Results of other researchers for both the H_2 and D_2 systems[13] are also shown in Fig. 1. Maier,[1] the first to study this system, "corrected" his experimental kinetic energy scale by 0.25 eV to make the apparent threshold agree with the known endothermicity $\Delta H_0^\circ = 0.398 \pm 0.003$ eV.[14] Fennelly[3] made the same energy correction. As can be seen in Fig. 1, the energy dependence of Maier's and Fennelly's results are in excellent accord with the present data when plotted on their original uncorrected energy scales. Koski and co-workers have published two sets of experimental data: An older set[2(a)] which is clearly in error and a newer set[2(b)] which is in better agreement with the present data (Fig. 1). In the latter case, our plot ignores an energy scale

correction of ~0.15 eV which was suggested.

In order to extract information about the true excitation function from the data, the experimental conditions which cause the apparent threshold to be lower than the thermodynamic endothermicity must be carefully evaluated. Chantry[15] showed that the random thermal motion of the reactant gas produces a significant broadening of the interaction energy, the so-called Doppler effect. This broadening depends on energy such that for this system it has a FWHM of 0.32 eV at the reaction endothermicity of 0.40 eV. The ion beam energy distribution in these experiments typically has a FWHM of 0.7 eV in the laboratory frame or 0.10 eV in the center-of-mass (c.m.) frame. The estimated uncertainty of the absolute energy scale determination is ± 0.1 eV lab or ± 0.015 eV c.m. In addition to these translational energy effects, internal excitation of the reactants can also lower the threshold. The C^+ ion beam has both $^2P_{3/2}$ and $^2P_{1/2}$ states but these are separated by only 64 cm^{-1} (0.008 eV).[16] Vibrational excitation of the H_2 reactant at 320 K is also negligible. The average rotational energy $\bar{E}_{rot}$ is 0.028 eV and there is a significant population up to the $J = 3$ level at 0.091 eV. Rotational enhancement, while not expected, would increase the effect of this energy on the apparent excitation function.

To ascertain the significant features of the true excita-
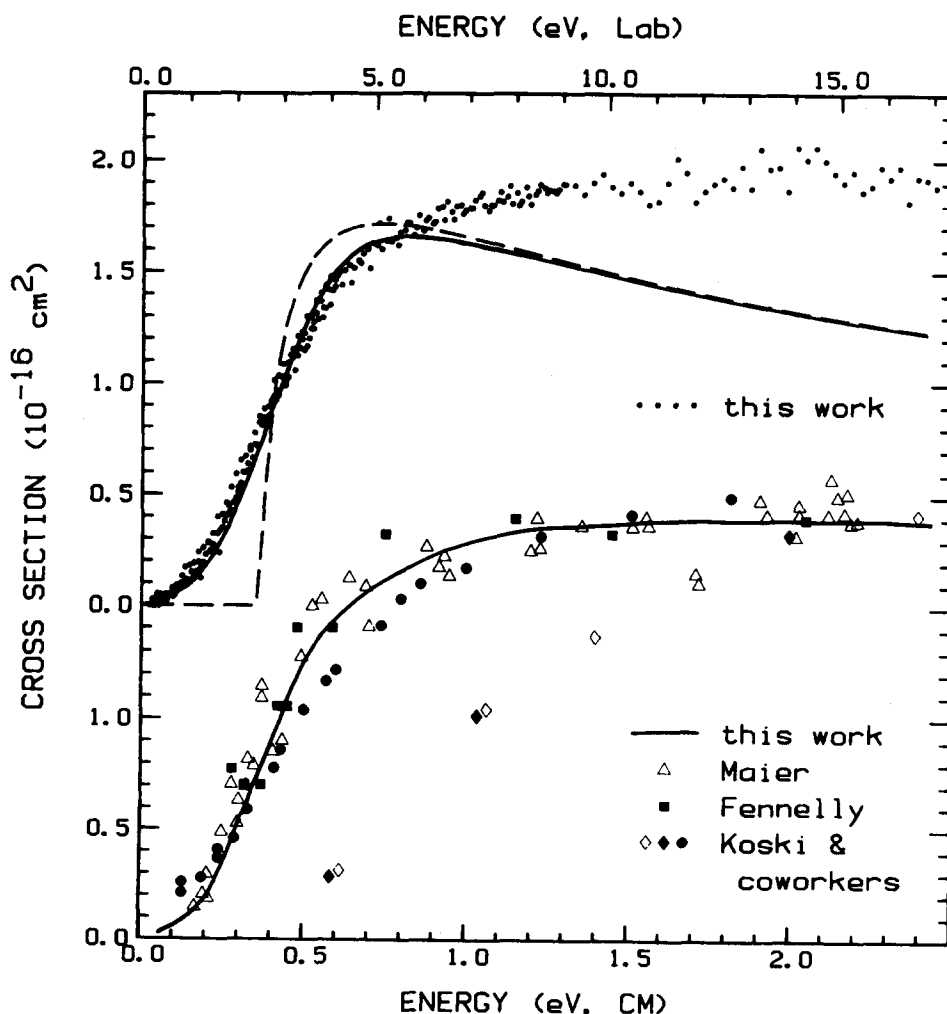

ENERGY (eV, Lab)

FIG. 1. Cross section for reaction (1) as a function of relative translational energy (lower scale) and laboratory energy (upper scale). The upper part, offset by 1.5×10^{-16} cm^2, shows experimental data from the present work and the unconvoluted (broken line) and convoluted (solid line) fit to the data described in the text. The lower part compares the present data, represented by the solid line, with literature results for reaction (1), solid symbols, and for the analogous process with D_2, open symbols. All results are plotted on uncorrected energy scales (see the text). Cross sections of Maier (Ref. 1) and Fennelly (Ref. 3) are reduced by 35% and 42%, respectively. Results of Koski and co-workers [diamonds, Ref. 2(a); circles, Ref. 2(b)] are as reported.

ENERGY (eV, CM)

tion function we convolute a trial form of the cross section with the Doppler and ion beam energy distributions for comparison with the data.[15,17] The cross section σ may be modeled[17,18] using the general form $\sigma(E) = \sigma_0(E - E_0)^n/E^m$, where E is the relative translational energy, E_0 is the threshold energy, and σ_0 is an energy-independent scaling factor. The exponents n and m may be allowed to vary as adjustable parameters or are determined by theory. In the fits described here, we have used $E_0 = \Delta H_0^\circ - \overline{E}_{rot} = 0.370$ eV, accounting in an approximate way for the H_2 rotational energy. A reasonable fit can be obtained by convoluting a form with $n = m \approx 0.25$ and $\sigma_0 = 2.0 \times 10^{-16}$ cm^2, which is essentially a rounded step function. While this fit is strictly empirical, it indicates that any theoretical treatment must account for both a very steep rise in the cross section at the threshold and the nearly flat energy dependence at higher energies. The familiar line-of-centers model, given by $n = m = 1$,[19] fails to achieve this as it rises too slowly in the threshold region. A form with $n = \frac{1}{2}$ and $m = 1$ can be derived using microscopic reversibility arguments and the long range ion-induced dipole potential.[20] This function $(\sigma_0 = 2.08 \times 10^{-16}$ cm^2 eV$^{1/2})$ and its convolution are compared with the data in Fig. 1. While this simple model decreases too rapidly above ~ 0.8 eV, it does exhibit the steep rise necessary to reproduce the threshold behavior. This confirms, at least for the present results, that the low apparent threshold can be explained without resorting to energy scale corrections. To our knowledge, this is the first case in which the ion-induced dipole form has been applied to the experimental threshold behavior of an endothermic reaction.

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