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# A crossed beam scattering study of reactions in the system acetylene cation–acetylene: formation of $C_2HD^{+\cdot}$ in $C_2D_2^{+\cdot} + C_2H_2$ and formation of $C_4H_3^+$ and $C_4H_2^{+\cdot}$ in $C_2H_2^{+\cdot} + C_2H_2$ collisions

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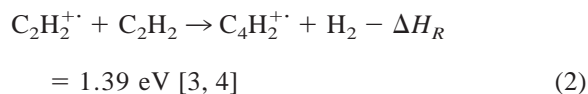
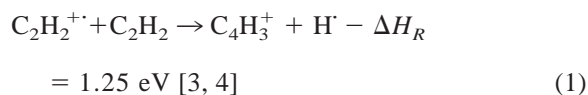
## Abstract

Dynamics of chemical reactions in the system acetylene cation-acetylene was investigated in crossed beam scattering experiments. Relative cross sections of formation of various products at  $T = 2.5$  eV were  $C_4X_3^+ : C_4X_2^+ : C_2X_2^{+\cdot} = 1.0:0.55:0.17$  ( $X = H, D$ ).  $C_2X_2^{+\cdot}$  ( $C_2HD^{+\cdot}$  from  $C_2D_2^{+\cdot} + C_2H_2$  collisions) traces the decomposition of an intermediate complex  $C_4X_4^{+\cdot}$  backward to reform the reactants; the mean lifetime of the intermediate is longer than about 5 ps and its geometry in the critical configuration close to linear. The products  $C_4H_3^+$  and  $C_4H_2^{+\cdot}$  are formed in exoergic reactions by the decomposition of a long-lived intermediate  $C_4H_4^{+\cdot}$  of prolate geometry in its critical configuration. About 15% of the energy available at  $T = 1.5$  eV in the latter two processes may be expected to be deposited as rotational energy of the product ion. (Int J Mass Spectrom 185/186/187 (1999) 195–205) © 1999 Elsevier Science B.V.

**Keywords:** Ion-molecule reactions; Collisional dynamics; Beam scattering; Intermediate complex formation

## 1. Introduction

Ion-molecule reactions between the acetylene cation and acetylene have been subjected to many studies and about two dozens of papers (see overview in [1]) appeared since the first study in the fifties [2]. The results on kinetics may be summarized in the following way: (1) The major products are  $C_4H_3^+$  and  $C_4H_2^{+\cdot}$  formed in exoergic processes in a ratio of about 2:1



(in addition, a minor channel giving  $C_2H_3^+$  was observed, endoergic with ground-state reactants); (2) H–D scrambling in the products formed in  $C_2H_2$ – $C_2D_2$  reactant mixtures suggests that a long-lived intermediate is involved in the formation of the  $C_4$  products.

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Dedicated to M.T. Bowers on the occasion of his 60th birthday, in appreciation of his contribution to the field of ion-molecule reactions.

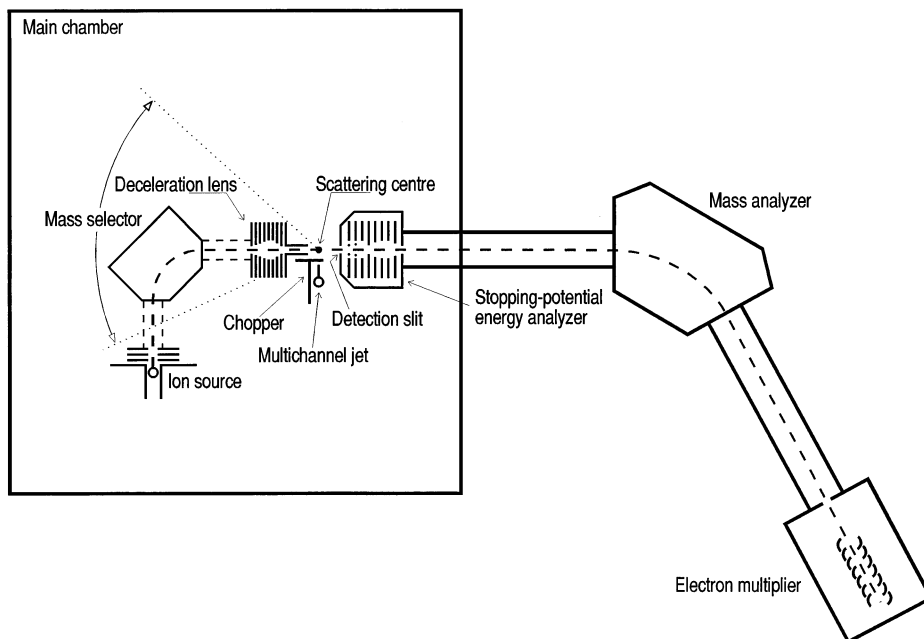
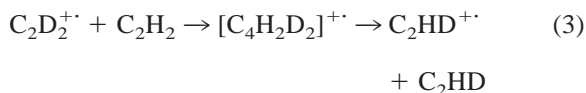


Fig. 1. Schematics of the apparatus EVA II.

Valuable information resulted from studies of reactions in the photoionized dimer  $(C_2H_2)_2$  [1, 5]. It established the ratio of rates of processes (2):(1) at ionization photon energies 11.4 through 20 eV and the role of excited acetylene cation in the product formation; from the photoionization thresholds the authors concluded that reaction (2) had an activation energy of about 12 kcal/mol, the activation energy of reaction (1) was close to zero. An important insight into the energetics and dynamics of  $C_4H_4^{+}$  was obtained from recent theoretical studies of the potential energy surface of  $C_4H_4^{+}$  [6–8], in particular the one which deals with the acetylene cation-acetylene reaction [8]. It provides a very detailed view of the energetics of the collision  $\pi$  complexes and  $C_4H_4^{+}$  isomers, transition states and activation energies connected with their interconversion. Unfortunately, it does not treat the decomposition channels to products of reactions (1) and (2).

We report here on a crossed beam scattering study of the acetylene cation-acetylene system, partly motivated by the above mentioned theoretical study of the potential energy surface. Reactions (1) and (2)

were studied in the collision energy range 1.5–2.5 eV [c.m. (center-of-mass)]. Besides that, using isotopic variants of acetylene, the backward decomposition of the intermediate complex to reform the reactants, namely the reaction



was investigated. Scattering diagrams, angular distributions and relative translational energy distributions were obtained and conclusions concerning the dynamics were drawn from them.

## 2. Experimental

The experiments were carried out on the crossed-beam scattering apparatus EVA II (Fig. 1). Briefly, reactant  $C_2H_2^{+}$  or  $C_2D_2^{+}$  ions were produced by impact of 120 eV electrons on acetylene or perdeuterio-acetylene gas, respectively, in a low pressure ion source. The ions were extracted, mass analyzed, and

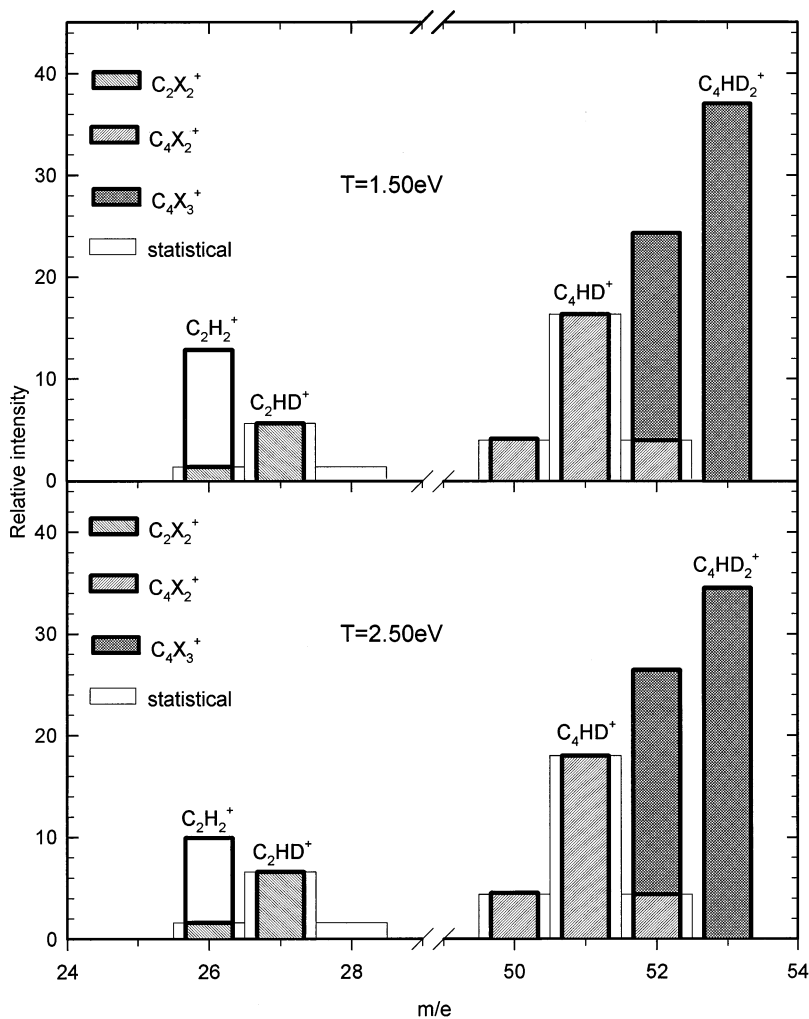


Fig. 2. Relative total cross sections for formation of  $C_2X_2^+$ ,  $C_4X_2^+$ ,  $C_4X_3^+$  ( $X = H, D$ ) in collisions of  $C_2D_2^+ + C_2H_2$  at collision energies 1.5 and 2.5 eV; thin line at  $C_2X_2^+$  and  $C_4X_2^+$  shows intensities of isotomers assuming statistical H/D scrambling.

decelerated by a multielement electrostatic lens system to a desired laboratory energy of a few eV. The ion reactant beam had an energy spread of about 0.2 eV [FWHM (full width at half maximum)] and an angular spread of about  $1^\circ$  (FWHM). The reactant beam was crossed at right angles by a thermal beam of the neutral acetylene molecules emerging from a neutral beam source. The source consisted of a multichannel jet and a collimation slit; the collimated beam had an angular spread of  $10^\circ$ , FWHM. The two beams could be rotated about the collision center in

the plane of the detector. Reactant and product ions passed through a detection slit, and they were energy analyzed by a stopping-potential analyzer, mass analyzed, and registered by a multiplier. Modulation of the neutral reactant beam, phase sensitive detection, and signal averaging was used to deal with background problems. Raw data consisted of angular distributions and sets of energy profiles of reactant and product ions at a series of scattering angles. The data were used to construct contour scattering diagrams of the product ion; the contours are given in

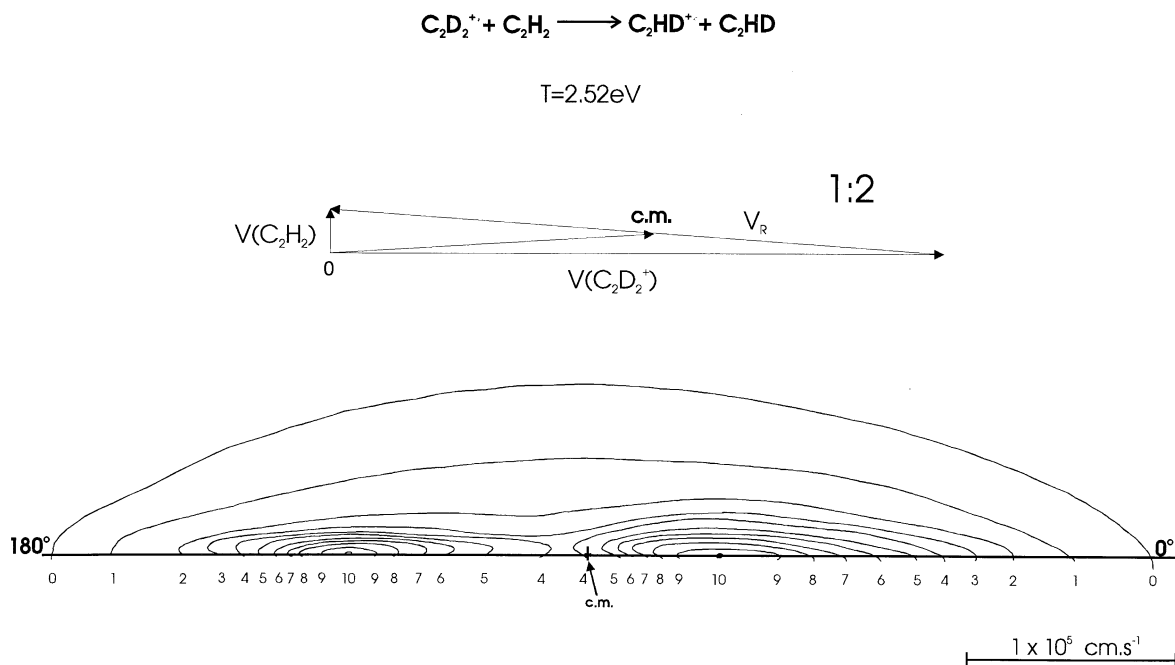


Fig. 3. Contour scattering diagram of  $\text{C}_2\text{HD}^+$  from reaction (3) at  $T = 2.52 \text{ eV}$ . The direction  $0^\circ$ – $180^\circ$  shows the relative velocity direction, c.m. marks the position of the center-of-mass of the system. Inset shows the respective Newton diagram (scale 1:2).

Cartesian probability  $P_{\text{CART}}$  [9]. Further dynamical quantities (relative differential cross sections,  $P(\vartheta)$  versus  $\vartheta$ , product relative translational energy distributions  $P(T')$  versus  $T'$ ), were obtained by appropriate integration of the scattering diagrams [9].

### 3. Results and discussion

#### 3.1. Relative total cross sections

Fig. 2 shows the relative total cross sections for various reactions occurring in the  $\text{C}_2\text{D}_2^+ + \text{C}_2\text{H}_2$  system for two collision energies, 1.5 and 2.5 eV (c.m.). The results were obtained by measuring the product intensities at the angular maximum and integrating them over the laboratory angular distribution. This, obviously, gives only approximate values, because the product distribution in the velocity space is not rigorously accounted for. The relative error was estimated to be about  $\pm 10\%$ , with the exception of the charge transfer channel ( $m/e = 26$ ). In the case of

$\text{C}_4\text{X}_3^+$  and  $\text{C}_4\text{X}_2^+$  ( $X = \text{H}, \text{D}$ ), the scattering diagrams are very similar and the distribution is concentrated close to the center-of-mass, for  $\text{C}_2\text{HD}^+$ —because of the forward-backward symmetry of the diagram—the inaccuracy largely compensates (see scattering diagrams).

The thin line in Fig. 2 for  $\text{C}_2\text{X}_2^+$  and  $\text{C}_4\text{X}_2^+$  shows contributions at a particular  $m/e$  assuming statistical H, D scrambling; the ratio of  $m/e$  51:50 indicates that the assumption of statistical contributions can be regarded as plausible. However, the formation of  $\text{C}_4\text{X}_3^+$  showed an isotope effect in favor of H-atom dissociation ( $\text{C}_4\text{H}_2\text{D}^+ : \text{C}_4\text{HD}_2^+ = 1.6$ – $1.8$ ). The ratio of products  $\text{C}_4\text{X}_3^+ : \text{C}_4\text{X}_2^+ : \text{C}_2\text{X}_2^+$  was 1.0 : 0.50 : 0.15 at 1.5 eV and 1.0 : 0.55 : 0.17 at 2.5 eV; the ratio  $\text{C}_4\text{H}_3^+ : \text{C}_4\text{H}_2^+$  is in fair agreement with the earlier findings [1]. The remaining part of  $m/e = 26$  evidently indicates charge transfer process via a simple electron jump without momentum exchange [10]. Its contribution to the overall branching ratio cannot be, however, estimated from these measurements, be-

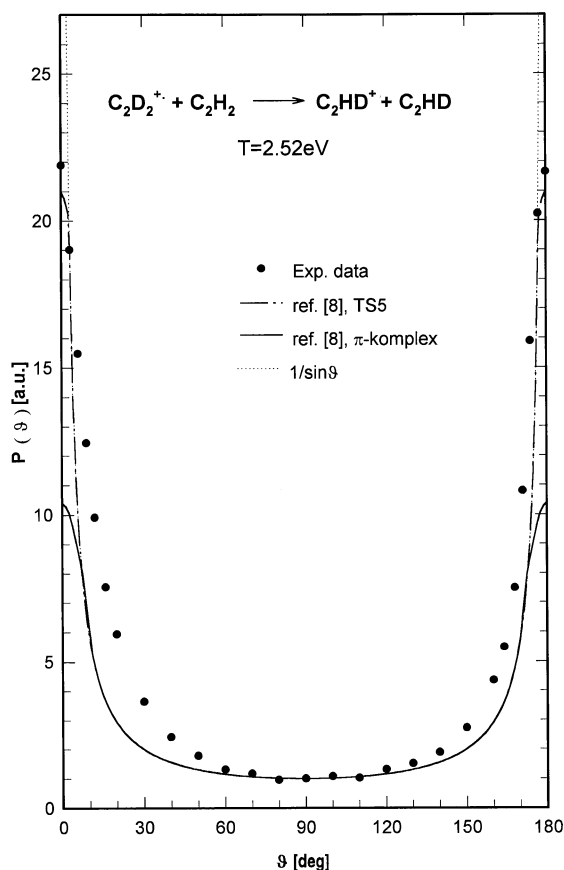


Fig. 4. c.m. angular distributions,  $P(\delta)$ , of  $C_2HD^+$  from reaction (3) at  $T = 2.52$  eV; full points—experiment; dashed—model calculations assuming linear geometry of the critical configuration; thin line—model calculation assuming critical configuration related to  $\pi$  complex; dotted—classical  $1/\sin(\delta)$  distribution.

cause the product may be expected to be scattered at small, close-to thermal velocities and the laboratory data strongly underestimate its contribution due to inconvenient form factors.

### 3.2. Scattering diagrams: $C_2HD^+$ formation

The scattering diagram of  $C_2HD^+$  from reaction between  $C_2D_2^+$  and  $C_2H_2$  [reaction (3)] at  $T = 2.52$  eV is shown in Fig. 3. The scattering exhibits a forward-backward symmetry and this indicates that  $C_2HD^+$  was formed as a result of decomposition of an intermediate species in which H–D scrambling

took place. Thus we can regard the process as a backward decomposition of an intermediate  $C_4H_2D_2^+$  to reform the reactants—a process that has to be taken always into account, if a long-lived intermediate complex is formed in a bimolecular elementary reaction. The fully developed symmetry of the scattering diagram suggests that the mean lifetime of the intermediate is longer than at least 5 mean rotations of such species. Using the usual model [10] we can estimate the average rotation of a linear (see further) intermediate as  $\bar{\tau}_R = 2\pi I_2 / \bar{L}$ , where  $\bar{L} = 2/3 L_{\max}$ . Assuming ion-induced dipole forces acting between the reactants,  $L_{\max} = 314 \hbar$  at the collision energy of 2.52 eV. The average rotation is then  $0.7 \times 10^{-12}$  s, and the mean lifetime of the collision species is longer than about  $4 \times 10^{-12}$  s. This is consistent with the existence of deep minima on the potential energy hypersurface of the system for various structures of  $C_4H_4^+$  [4]. The c.m. angular distribution, derived from the scattering diagram and shown in Fig. 4, exhibits a prominent peaking at  $0^\circ$  and  $180^\circ$ . This suggests an intermediate which is practically linear in the critical configuration. (We identify the critical configuration of the dissociating intermediate with the transition state on the way to the products which dissociates by extension of a critical bond.) The dashed line and the solid thin line in Fig. 4 show our model calculations of the angular distributions assuming two geometries of the critical configuration as obtained in the ab initio theoretical calculations (see Fig. 12 in [8])—a practically linear transition state (TS5 in [8]) and a transition state connected with the formation of a  $\pi$  complex (TC in [8]), respectively. The angular resolution of this experiment in the center-of-mass was about  $2.5^\circ$  (FWHM).

As in our earlier work [12, 13], our calculations use the classical statistical complex decomposition model of Miller, Safron and Herschbach [11], applied to ion-molecule reactions. The model calculations assume: (1) The complex is formed for all impact parameters  $0 \leq b \leq b_{\max}$  from reactants moving in the ion-induced dipole force field; at  $T = 2.52$  eV this gives  $L_{\max} = 314 \hbar$ . (2) The rotational temperature of the intermediate is the same as its vibrational temperature,  $T_R^* = T_V^* = E_{\text{tot}}/k_B(3N - 6) =$

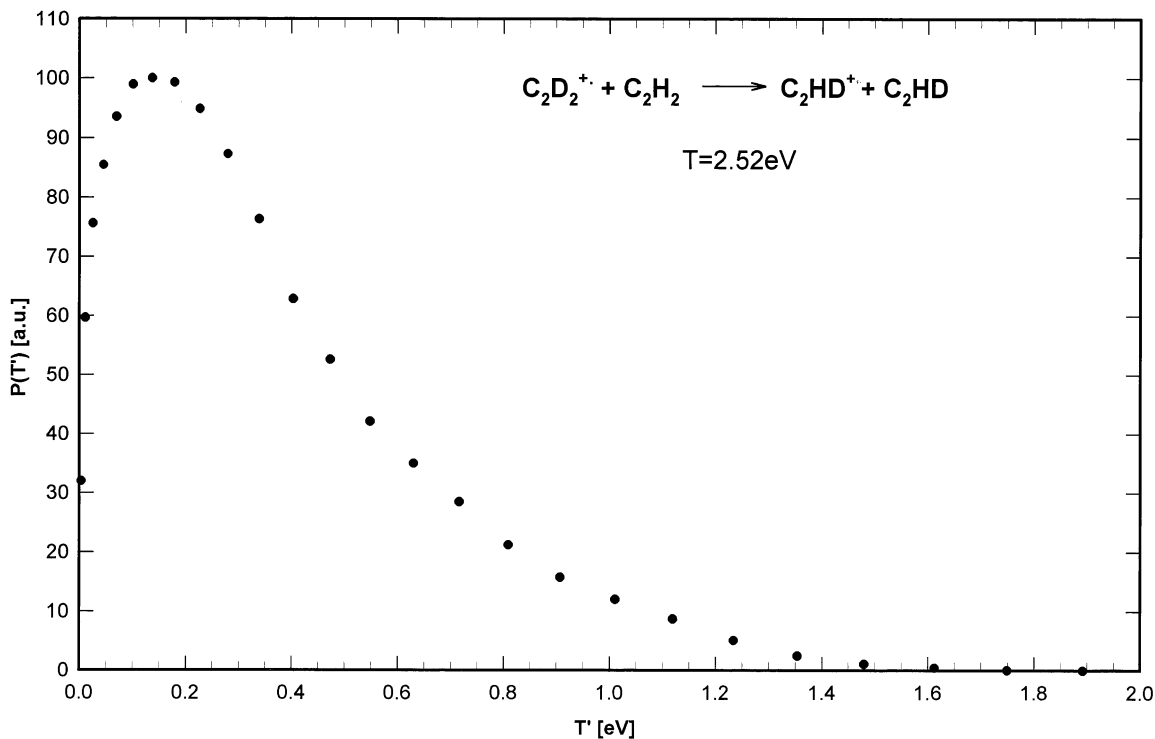


Fig. 5. Relative translational energy distribution,  $P(T')$ , of products of reaction (3) at  $T = 2.52$  eV.

1690 K [ $E_{\text{tot}} = T + E_{\text{int}} + (-\Delta H_R) = 2.62$  eV for collision energy  $T = 2.52$  eV, average internal energy of the ion reactant  $E_{\text{int}} = 0.1$  eV, and a thermoneutral reaction,  $k_B$ —Boltzmann constant,  $N$ —number of atoms in the system]. (3) The complex in its critical configuration may be regarded as a near-symmetric top dissociating to products along its principal axis, with moments of inertia  $I_1$  (along its principal axis) and  $I_2$  (perpendicular to it); the moments of inertia are derived from the geometry of the critical configuration.

It can be seen that the shape of the angular distribution agrees reasonably well with the near-linear geometry of the transition state TS5. The shallow well of the  $\pi$  complex presumably does not play a significant role in the dissociation of the intermediate backward to the reactants at this fairly high collision energy.

Fig. 5 shows the relative translational energy distribution of the products of this reaction channel.

Its peaking at a very low energy 0.13 eV (about 1/20 of  $E_{\text{tot}}$ ) is in general consistent with a process involving formation of a statistical intermediate. A quantitative comparison with model calculations was hampered by difficulties in analyzing the scattering data for other reaction channels.

### 3.3. Scattering diagrams: formation of $C_4H_3^+$ and $C_4H_2^+$

Scattering diagrams of  $C_4H_3^+$  and  $C_4H_2^+$  formed in reactions (1) and (2) are given in Fig. 6 and 7, respectively, at two collision energies 1.5 eV and 2.5 eV. In all cases the product peaks practically at the center-of-mass point and the diagrams exhibit a slightly elongated shape along the relative velocity axis.

The product is concentrated closely about the center of mass. This is a result of a very unfavorable kinematics: because of a high ratio of the product masses, 51:1 and 50:2 for reactions (1) and (2),

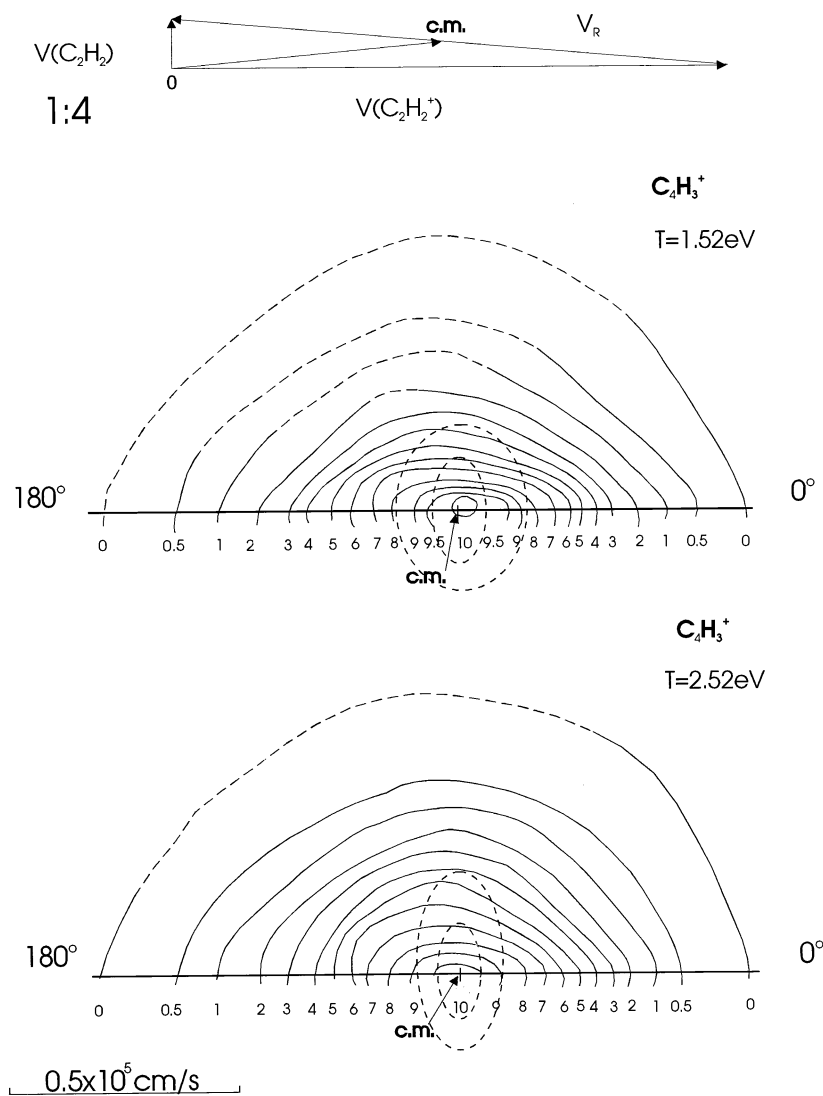


Fig. 6. Contour scattering diagrams of  $C_4H_3^+$  from reaction (1) at  $T = 1.52$  eV and  $T = 2.52$  eV. Inset shows the respective Newton diagram for  $T = 1.52$  eV (scale 1:4); O—position of the LAB origin; c.m. indicates the position of the center-of-mass of the system; dotted contours: scatter of the center-of-mass due to spreads in beams (see text).

respectively, conservation of linear momentum leads to a low recoil velocity of the heavy ion product in the c.m. coordinates. The recoil velocity of a large fraction of the ion product is then located close to the center-of-mass, and it is thus comparable to the scatter of the positions of the tip of the center-of-mass velocity vector because of an experimental inaccuracy, namely to energetic and angular spreads in the

beams (shown by dashed contours in Figs. 6 and 7). Both c.m. angular distributions and the product relative translational energy distributions are influenced by this factor.

The c.m. angular distributions show peaks of uneven height at  $0^\circ$  and  $180^\circ$ , about 2–4 times higher than the  $I(\vartheta)$  value at  $90^\circ$ . This suggests decomposition of an intermediate complex, prolate in its critical

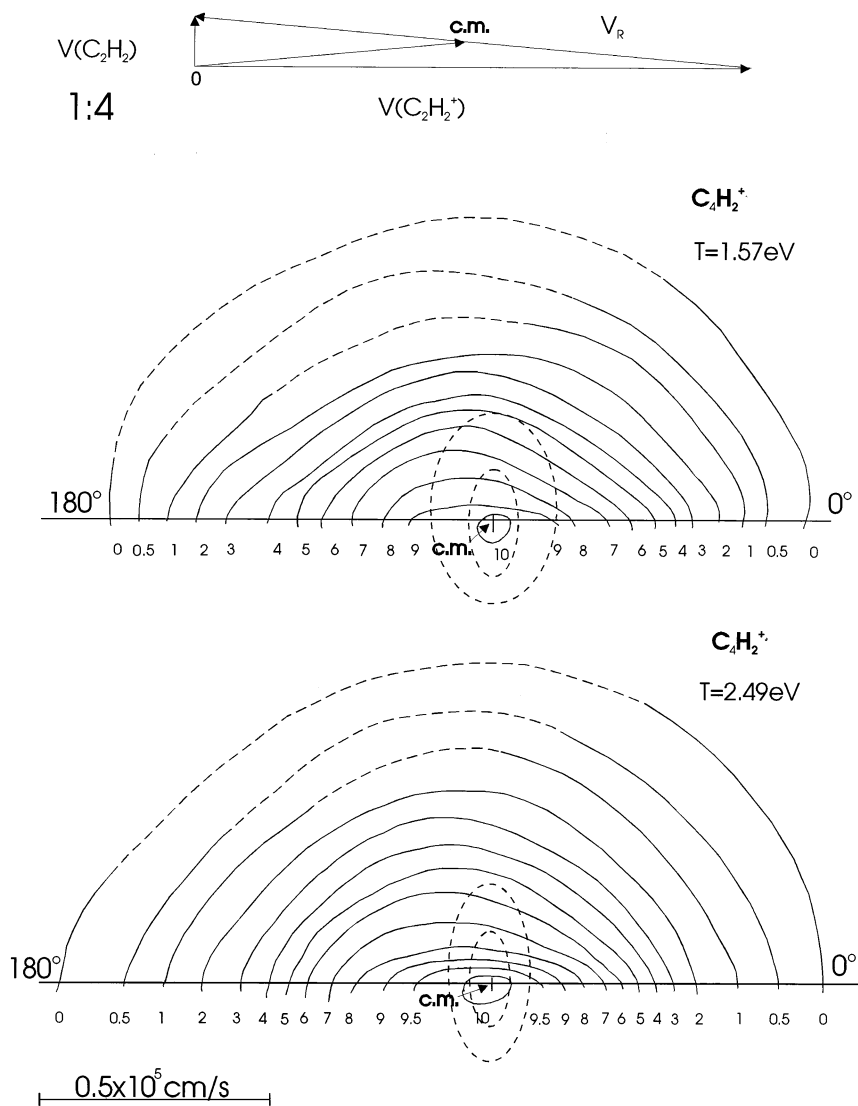


Fig. 7. Contour scattering diagrams of  $C_4H_2^+$  from reaction (2) at  $T = 1.57$  eV and  $T = 2.49$  eV. Inset shows the respective Newton diagram for  $T = 1.57$  eV (scale 1:4); O—position of the LAB origin, c.m. indicates the position of the c.m. of the system; dashed contours: scatter of the center-of-mass due to spreads in beams (see text).

configuration. However, more detailed analysis is difficult to perform: the convolution of the spread of the center-of-mass into the tight distribution of the product about the c.m. point influences in particular the intensity at scattering angles about  $90^\circ$ . Also, slight inaccuracies in determining the exact positions of low  $P_{\text{CART}}$  contours (especially likely in the backward direction) in Figs. 6 and 7 can be grossly

magnified in the  $I(\vartheta-\vartheta)$  plots; the seemingly well symmetric diagrams then yield very uneven peaks at  $0^\circ$  and  $180^\circ$  in Figs. 8(a) and (b). The conclusion concerning the prolate shape of the dissociating intermediate is qualitatively consistent with information on energetics and structures inferred from neutralization-reionization experiments on isomerization and dissociation of  $C_4H_4^+$  radical ions [3]: dissociation to



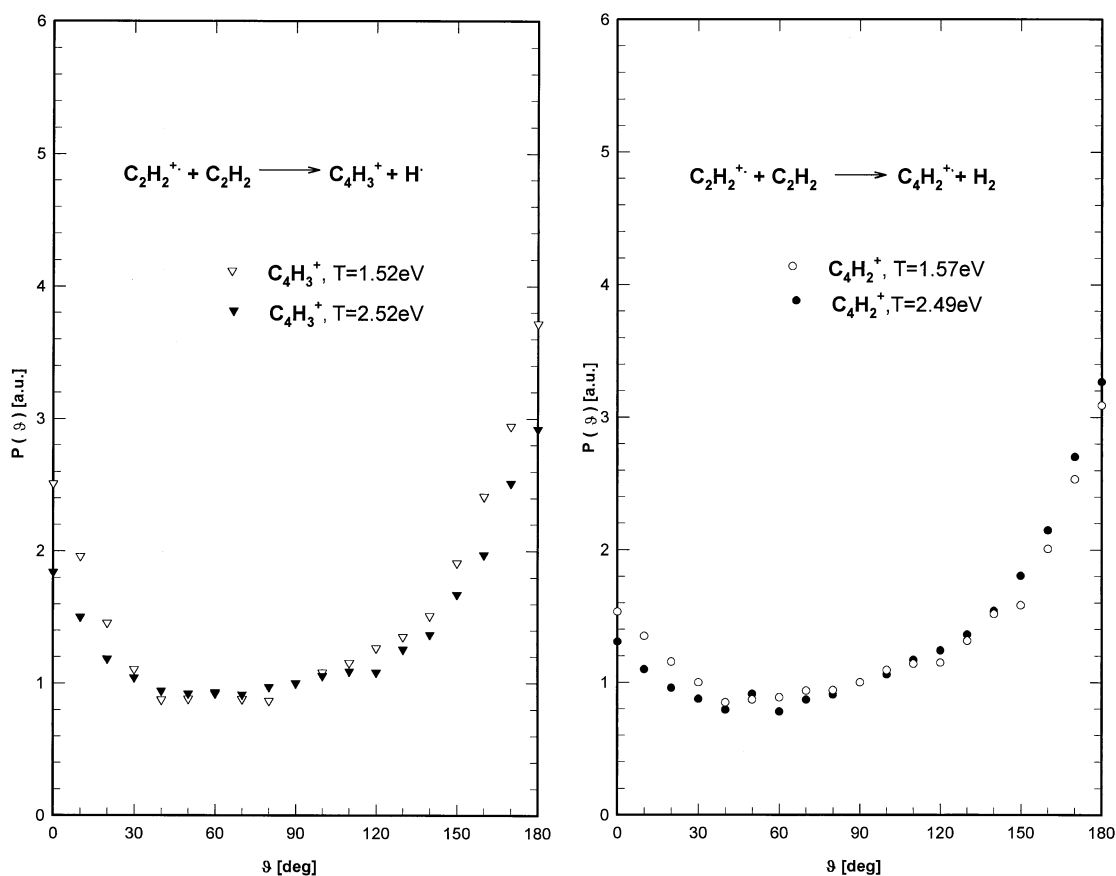


Fig. 8. c.m. angular distributions,  $P(\vartheta)$ , of (a)  $C_4H_3^+$  from reaction (1) at 1.52 eV (open inverted triangle) and 2.52 eV (filled inverted triangle), (b)  $C_4H_2^+$  from reaction (2) at 1.57 eV (○) and 2.49 eV (●).

$C_4H_3^+$  and  $C_4H_2^+$  is assumed to occur from a (practically linear) vinylacetylene cation precursor by splitting off H or  $H_2$ , respectively.

The product relative translational energy distribution,  $P(T')$ - $T'$  plots in Figs. 9(a) and (b), show peaking at 0.35–0.5 eV. This peak at a rather high energy may be possibly caused by an exit barrier on the way to the reactants (activation energy for the reverse reaction) suggested for reactions (1) and (2) from other studies: “very small” and 0.5 eV [1] or about 0.85–1 eV [3]. However, the inaccuracies because of kinematic effect are here quite serious, too. The recoil velocity of the heavy ion corresponding to the peak in the  $P(T')$  distributions is still within the spread of the center-of-mass and thus no definite conclusion about the low-energy (0–0.5 eV) part of the

$P(T')$  curves can be made. The evaluation procedure strongly accents the contributions from the region of low intensity contours and small inaccuracies there are reflected in the  $P(T')$  curves which, because of the kinematic factor, tail to very high energies, beyond the limits of total energy available in the process [arrows in Figs. 9(a) and (b)], especially in case of reaction (1).

An interesting conclusion can be made about the fate of the rotational energy in reactions (1) and (2). There is a large difference between the reduced mass of the reactants ( $\mu = 13.0$ ) and products ( $\mu'(1) = 0.98$ ;  $\mu'(2) = 1.92$ ). Conservation of angular momentum in a reactive collision requires

$$J_{\text{tot}} = L + J = L' + J' \quad (4)$$

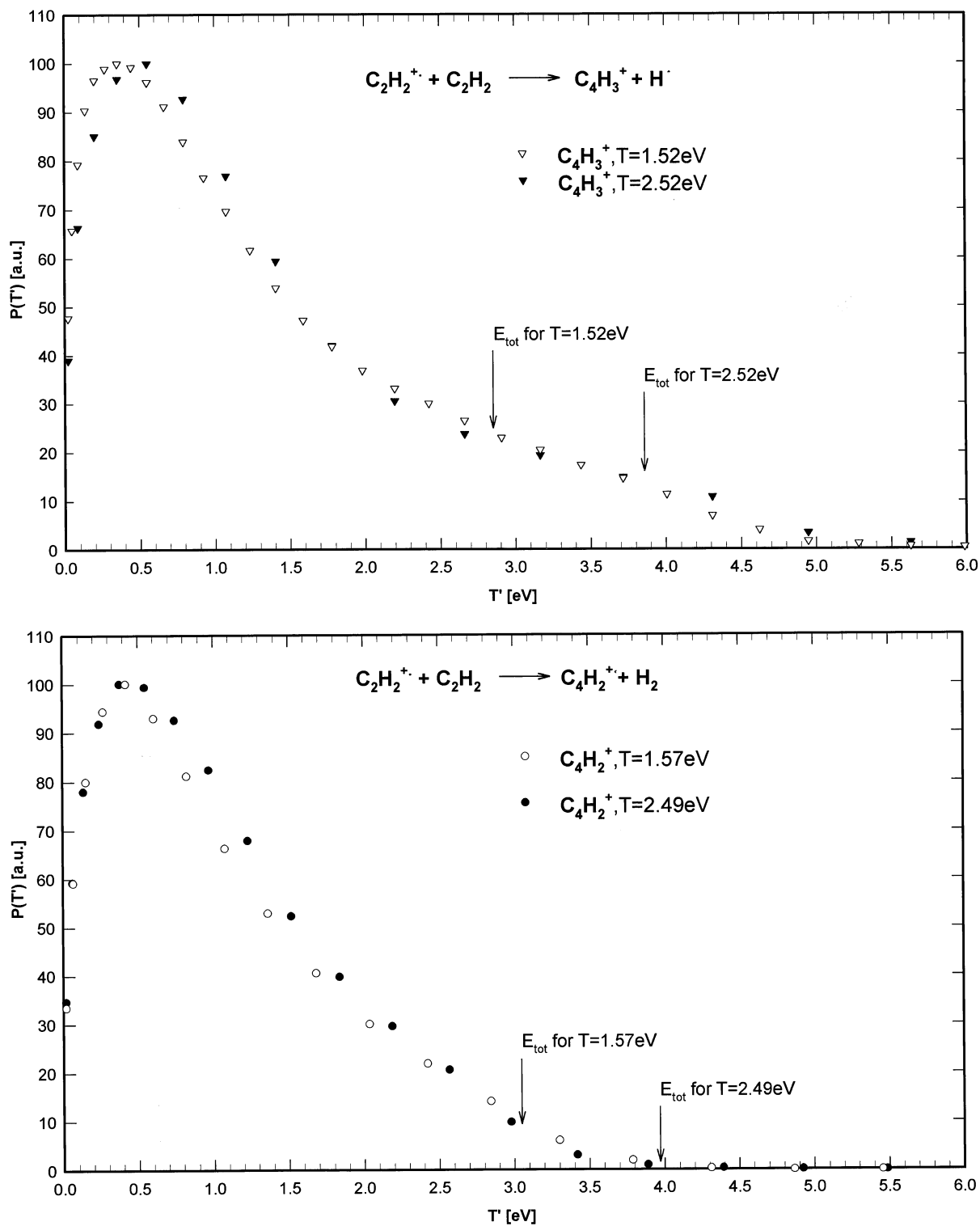


Fig. 9. Relative translational energy distributions of products of (a) reaction (1) at 1.52 eV (open inverted triangle) and 2.52 eV (filled inverted triangle), (b) reaction (2) at 1.57 eV (open circle) and 2.49 eV (filled circle). Arrows indicate total energy available in the process,  $E_{\text{tot}} = T + E_{\text{int}} + (-\Delta H_R)$ .

where  $L = \mu v_R b$  is the orbital angular momentum of the reactants ( $\mu$ -reduced mass,  $v_R$ -relative velocity,  $b$ -impact parameter), and  $J$  is the sum of rotational momenta of the particles in question; primed quantities refer to products. The rotational momenta of the reactants,  $J$ , are approximately thermal and can be neglected with respect to  $L$ :  $L_{\max} = 277 \hbar$  for  $T = 1.5$  eV, average  $\bar{L} = 2/3 L_{\max} = 185 \hbar$ . Because  $\mu' \ll \mu$ , the product orbital angular momentum  $L' \ll L$ , if we assume that  $v'_R \cong v_R$  and  $b' \cong b$ . Then

$$J_{\text{tot}} = L = J' \quad (5)$$

i.e. most of the originally orbital angular momentum of the reactants should remain as rotational momentum of the polyatomic ion product. Approximate estimations show that at the collision energy of 1.5 eV, the average fraction of the available energy which remains as the ion product rotational excitation for reactions (1) and (2) (exoergic by about 1.3 eV) is about 0.5 eV ( $\cong 15\%$  of the total available energy  $E_{\text{tot}} = 2.9$  eV).

#### 4. Conclusions

Dynamics of formation of  $\text{C}_2\text{HD}^{+\cdot}$  in collisions of  $\text{C}_2\text{D}_2^{+\cdot} + \text{C}_2\text{H}_2$  was investigated in a crossed beam experiment at a collision energy of 2.5 eV. The product was formed by a decomposition of a long lived intermediate  $\text{C}_4\text{H}_2\text{D}_2^{+\cdot}$  of an average lifetime longer than about 5 ps. The c.m. angular distribution of the product, peaked strongly at  $0^\circ$  and  $180^\circ$ , suggested that the geometry of the critical configuration of the dissociating complex was close to linear and consistent with a linear transition state described in a theoretical study of the  $\text{C}_4\text{H}_4^{+\cdot}$  hypersurface.

Scattering studies of the formation of the reaction products  $\text{C}_4\text{H}_3^+$  and  $\text{C}_2\text{H}_2^{+\cdot}$  in collisions of  $\text{C}_2\text{H}_2^{+\cdot}$  and  $\text{C}_2\text{H}_2$  showed that the products were formed by a decomposition of a long-lived intermediate, prolate in its critical configuration; this indicates that the prod-

uct ions have an open chain rather than cyclic structure. Detailed analysis of the data was obstructed by an unfavorable kinematics of a heavy ion product recoiling on a very light neutral reactant partner. Conservation of angular momentum implies that a substantial fraction of the energy available in the reactions remains as rotational excitation of the product polyatomic ion.

#### Acknowledgement

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