

Binding energy of H_3^+ from the analysis of angular and energy distributions of the reaction $\text{H}_3^+ + \text{He} \rightarrow \text{H}_2^+ + \text{H} + \text{He}$

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(Received 14 April 1987; revised manuscript received 17 July 1987)

We have applied both angular and energy distribution measurements of the collision-induced dissociation of a-few-keV H_3^+ in He to estimate the binding energy of the triatomic molecular ion H_3^+ . Our measured value of 6.3 ± 0.5 eV below the dissociation energy agrees well with previous theoretical predictions and experiment.

It is known from theoretical calculations and experimental studies that the ground state $^1A'_1$ of H_3^+ has an equilateral triangle structure with sides of 1.65–1.66 a.u. and that the calculated binding energy is at 1.34–1.35 hartrees.^{1,2} At keV energies, the binding energy of the ground state of H_3^+ in its lowest vibrational level has been determined experimentally by Goh and Swan³ from an analysis of the energy spectra of the H_2^+ fragments resulting from the excitation of H_3^+ particles in collisions with He. However, from the analysis of our laboratory-frame (LF) distributions, we have found that the identification of the energy values at which the intensity goes to a minimum, from which the binding energy can be evaluated, is a difficult and rather uncertain procedure. In fact, a very small variation on the estimation of these limits produces a considerable modification in the resulting internal energy increase on the system E .

Because of the correlation between center-of-mass energy distributions of the dissociating fragments and their angular spread in LF, it is possible to use the results from both measurements to estimate the binding energy of a molecular projectile when the two-step model of excitation, followed by binary dissociation is assumed. The correlation of the results from angular and energy distributions also supports the internal consistency of the final results.

The experimental apparatus has been described in detail elsewhere.^{4,5} Molecular ions of mass $(M+m)$, formed in a Colutron-type ion source were electrostatically accelerated at energies of 1.25, 2.75, 3.5, and 4.83 keV. The selected molecular ion beam was velocity analyzed by a Wien filter, passed through cylindrical plates to deviate it by 10° , and through a series of collimators before it entered the gas target cell, which was a cylinder of 2.5 cm in length and diameter, with a 1-mm entrance aperture, and a 2-mm-wide, 6-mm-long exit aperture. All apertures and slits had knife edges. The target cell was located at the center of rotatable, computer-controlled vacuum chamber that moved the whole detector assembly 47 cm away from the target cell. The detector assembly consisted of a Harrower-type parallel-plate analyzer,⁶ with a channel electron multiplier (CEM) attached to its exit end, the beam entering the

uniform electric field at an angle of 45° . This analyzer was used to measure both angular and energy distributions of the products by replacing its entrance collimators. To measure the angular distributions, a 0.36-mm diameter pinhole was located at the entrance of the analyzer and a 1-cm orifice was placed in front of the CEM, while a slit 1-cm-long and 0.01-mm-wide was placed in front of the CEM for energy distribution measurements. Path lengths and apertures gave an overall angular resolution of the system of 0.1° . The energy distributions were obtained by varying the voltage of the analyzer, its calculated energy resolution being $\Delta E/E = 4.5 \times 10^{-3}$.

The data were analyzed by using the relations

$$(M+m)U = M(V-W-E) + mW \pm 2[MmW(V-W-E)]^{1/2}, \quad (1)$$

$$\theta_{\max} \simeq [mW_{\max}/M(V-W_{\max}-E)]^{1/2}, \quad (2)$$

$$(m/MV) \left(\frac{d\sigma}{d\Omega} \right) = f[(M/m)V\theta^2]. \quad (3)$$

Equation (1) refers to energy distributions, whereas Eqs. (2) and (3) refer to angular distributions. In Eq. (1), U is the final energy of the fragment of mass M detected at an angle of 0° in LF, V is the initial energy of the molecular projectile of mass $(m+M)$, E is the internal energy increase of the system, and W is the kinetic energy released as a result of the dissociation process. The \pm signs correspond to forward or backward ejection of the fragment of mass M .⁷ An energy spectrum at 3.5 keV is shown in Fig. 1. In Eq. (2), θ_{\max} is the angle between the direction of the observed fragment (M) and the incident beam direction at which the angular spread is a maximum. θ_{\max} is in turn related to the maximum kinetic energy W_{\max} at which the fragments are released. θ_{\max} is shown in Fig. 2 for three different energies. Equation (3) represents a scaling law that relates the angular distributions for different incident energies V ; $d\sigma/d\Omega$ is the absolute differential cross section and θ is the angle between the observed fragment and the incident beam direction.⁴ It has been shown^{4,5} that for

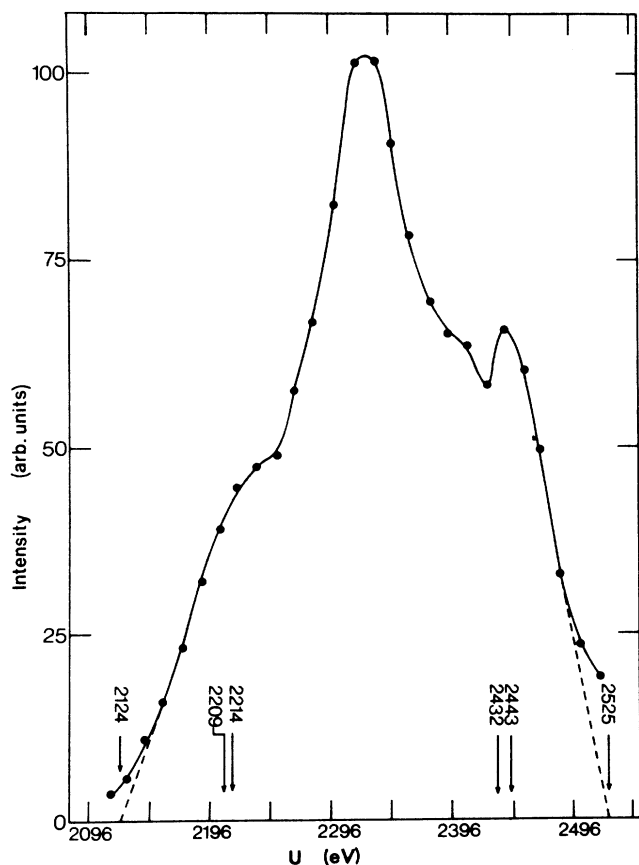


FIG. 1. LF energy spectrum of the H_2^+ fragment at 3.5 keV of H_3^+ .

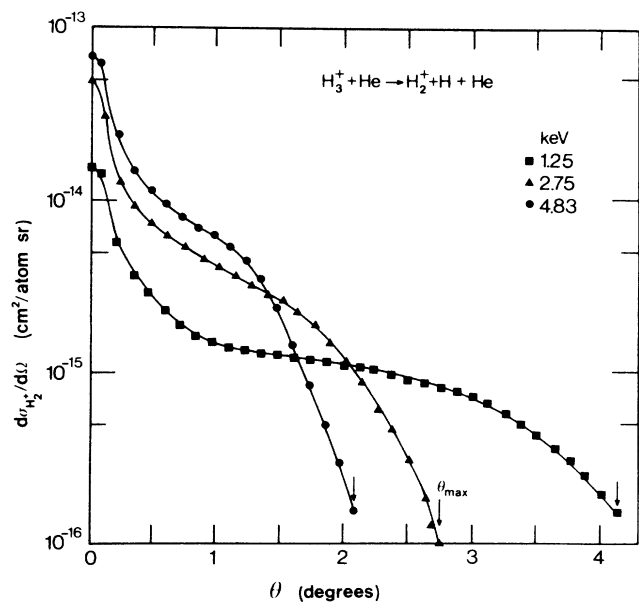


FIG. 2. Angular distributions of the H_2^+ fragment, showing θ_{\max} . Each curve is the average of several runs after a careful subtraction of the background. The angular resolution of the apparatus is 0.1° .

any fragment arising from a velocity-independent process such as electronic excitation, the left side of Eq. (3) is a universal function of $(M/m)V\theta^2$. This result arises from the following five assumptions,^{4,5} namely, that (i) the electronic excitation is faster than vibrational and rotational motions, (ii) rotational energies are negligible in comparison with dissociation energies, so that the dissociation direction is that of the line joining the two fragments, (iii) all orientations are equally probable, (iv) dissociation energies are small in comparison with the incident beam energy, and (v) the deflection of the center of mass of the molecular ion is negligible due to electronic excitation. Notice that the above assumptions are essentially the same as those supporting the validity of the two-step model in the keV region.⁸ From Eqs. (1) and (2) we can relate the results from both angular and energy distribution measurements. The angular distribution of the dissociation products is due entirely to the transverse component of the dissociation energy of the fragment. Thus, with the observed θ_{\max} on the angular distributions, and provided that $V \gg W_{\max} + E$, then W_{\max} is evaluated from Eq. (2), and this value must be the same as that derived from Eq. (1) by taking the energy values at which the intensity goes to a minimum on the energy spectra. As was pointed out in Ref. 3, the maximum $E + W$ ensures that the excitation originates in the lowest vibrational level of H_3^+ , and the maximum in W ensures the minimum residual internal energy.

The spectra of dissociation energies in collision-induced dissociation rarely consist of sharp lines, and the excitation cross sections depend strongly on the instantaneous separation R_{mM} of the molecular constituents M and m at the time of collision. Very often, the spectrum of dissociation energies consists of broad structures or shoulders due to the distribution of vibrational energies in which the projectile enters the collision. A similar explanation holds for angular distributions. The data were treated through an iteration method by taking the energies corresponding to the minimum intensity limits on the energy spectra as testing values, comparing the corresponding W and E for the two branches of the spectra, and then comparing this W value with the W_{\max} as derived from the angular distribution. Finally, the best E and W values consistent with both angular and energy distributions were obtained. In the energy spectrum of Fig. 1, the values of $U_1 = 2124$ eV and $U_2 = 2525$ eV at which the intensity goes to a minimum were chosen, from the angular distributions (Fig. 2) a corresponding W_{\max} was chosen, and then, the E and W values calculated from this method were

$$W = 13.0 \pm 1 \text{ eV}$$

and

$$E = 6.3 \pm 0.5 \text{ eV} .$$

These energy values were plotted in Fig. 3.

In the energy distribution of Fig. 1, a broad structure can be seen around $U_1 = 2214$ and $U_2 = 2443$ eV. With these particular energy limits, values of $W = 4.2 \pm 0.32$ eV and $E = 5.0 \pm 0.4$ eV are obtained. Inserting these values

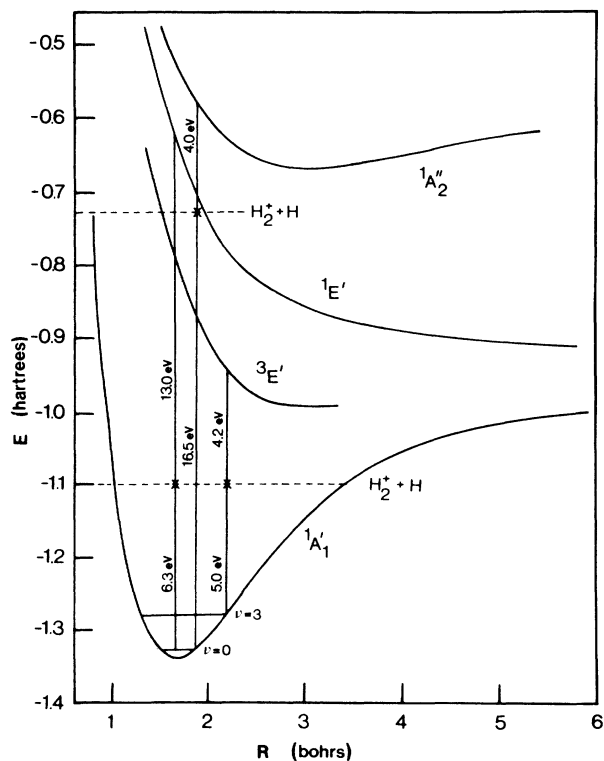
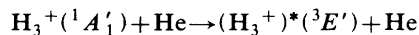
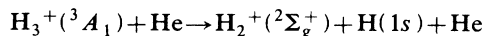


FIG. 3. Relevant H_3^+ potential-energy curves in D_{3h} symmetry (equilateral structure). R is the length of the side of the triangle. Dotted lines show the dissociation limits (from Ref. 1).

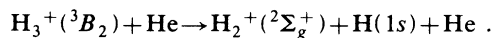
in the potential-energy curves of Fig. 3, a transition from the $H_3^+(^1A_1')$ state with a vibrational quantum number $v \approx 3^{10}$ to the $H_3^+(^3E')$ state at $R=2.16$ bohr is observed. The $^3E'$ state is repulsive, and since it is known that when H_3^+ undergoes a small distortion from the D_{3h} to the C_{2v} symmetry due to a collision, it then splits into the 3A_1 and 3B_2 states, thereby producing H_2^+ as a charged fragment.⁹ Hence we interpret this transition as coming from the reaction channel,



to



or



On the other hand, using slightly different values of $U_1=2209$ eV and $U_2=2432$ eV, we obtain $W=4.0 \pm 0.3$ eV and $E=16.5 \pm 1.4$ eV. As seen in Fig. 3, this indicates another possible reaction channel,

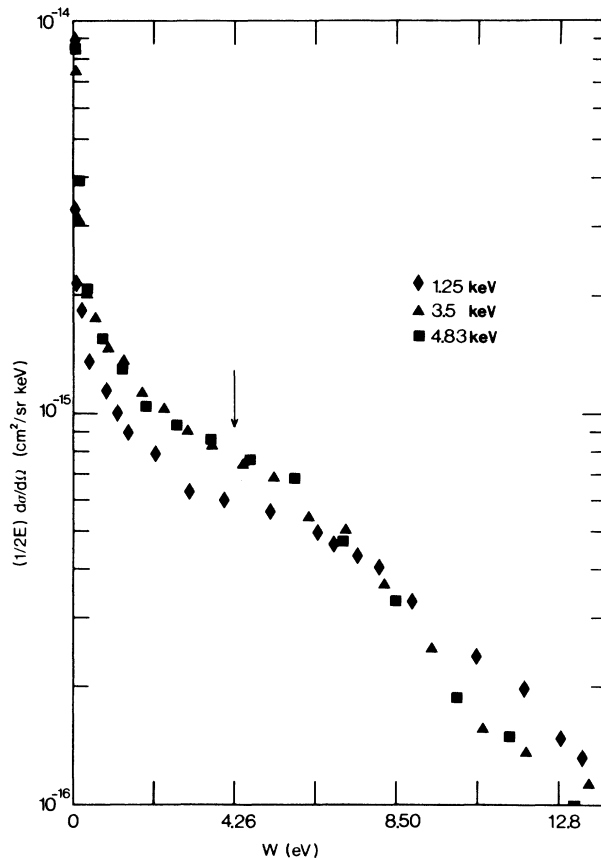
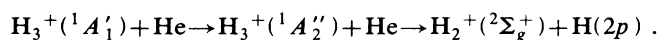


FIG. 4. Single-run scaled angular distribution. Horizontal axis shows the W energy values derived from Eq. (2).

Replotting the angular distributions in terms of the scaled variables,^{4,5} it can be seen that they follow the same scaling law. Then it is reasonable to interpret that over this energy range, the same processes are taking place. Figure 4 shows the scaled angular distributions, where an approximate value of $W=4$ eV corresponds to the inflection point, which in turn corresponds to the identified channels from the energy distribution.

In conclusion, a binding energy of 6.3 ± 0.5 eV for the H_3^+ molecule has been determined experimentally by analyzing both angular and energy distributions from the reaction H_3^+ in He. The present value is the same as that reported by Goh and Swan,³ whereas the rather high uncertainty in our value is mainly due to the angular resolution of the apparatus. However, the method used herein reduces the ambiguity in the assignment of the energy limits when only the energy distribution is available. Additionally, plotting the angular distributions in terms of reduced variables sheds more light on the validity interval of the dissociation models by recognizing that the same process is operative at different energies.

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