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Observation of an electronically excited state of H_3 and determination of its vibrational level structure

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Discrete energy levels of H_3 are observed by measuring the translational-energy spectrum of H-H_2 fragment pairs arising from predissociation of H_3. The translational-energy spectrum exhibits structure in the range from 3.5 to about 6 eV. The excited H_3 molecules are obtained in electron-capture collisions of 10-keV H_3^+ ions on H_2. The H_3^+ ions are produced in an electron-impact ion source at high hydrogen pressure. The translational-energy spectrum of H-H_2 fragment pairs is measured with a flight-time-difference method. The energies and intensities of the observed peaks are compared with calculations by Porter. The observed levels can be attributed to vibrational levels in the upper Jahn-Teller sheet of H_3. The spectrum can be described very well using the following parameters: The ground vibrational level in the upper Jahn-Teller sheet lies at 3.50 eV above $H+H_2$ in its ground vibrational level. The vibrational quanta are 0.32 and 0.49 eV for the breathing and degenerate vibrations, respectively.

I. INTRODUCTION

In a preceding paper[1] we reported measurements of two-dimensional velocity distributions of H-H_2 fragment pairs resulting from collisions of 10-keV H_3^+ ions on H_2. The dependence on ion-source gas pressure was studied. The main part of the velocity distributions could be explained by dissociative electron capture into the repulsive electronic ground state of H_3. A small step which appeared in the fragment velocity distribution for vibrationally deexcited H_3^+ indicated, however, that predissociation of a bound excited state of H_3 contributes to the formation of H-H_2 fragment pairs.

When energy levels of bound excited molecular states are predissociated by repulsive states, discrete energies in the fragment translational-energy spectra are to be expected. The efficiency of our flight-time-difference method in resolving the vibrational structure of predissociated states has been demonstrated[2,3] for H_2. Now, these high-resolution measurements have been extended to H_3 formed by electron capture of H_3^+. The vibrational structure found in the translational-energy spectra of H-H_2 fragment pairs will be compared with theoretical predictions given by Porter.[4]

II. EXPERIMENT

The H_3^+ ions were produced in an electron-impact ion source at high pressure. The hydrogen gas pressure was about 1.0 mbar. The electrons were accelerated by 40 V. The current between the filament and the electron collector was about 2 mA. No potential was applied between the ionization region and the exit aperture of the ion source. The exit aperture was 0.15 mm in diameter, thus ensuring a strong pressure gradient. The extracted H_3^+ ions are thought to be in their vibrational ground state.[5,6] The ratio $I_{H_2^+}/(I_{H_3^+}+I_{H_3^+})$ was 0.015, where $I_{H_2^+}$ and $I_{H_3^+}$ are the H_2^+ and H_3^+ ion currents drawn from the ion source. The H_3^+ ion current, measured behind a collimating aperture of 0.8-mm diam., was about 5×10^{-10} A.

The ions were accelerated to 10 keV, mass analyzed, and fired through a collision chamber which was filled with hydrogen gas at 1×10^{-3} mbar. The collision chamber was 1.0 cm long. Thus the conditions for single collisions were fulfilled. This was also checked by changing the pressure in the collision chamber. The H and H_2 fragments arising from dissociative electron capture of H_3^+ were detected by two detectors in coincidence with respect to their flight-time difference and flight direction. Electrostatic lenses were used to reject charged particles. The distance between the collision chamber and the detectors is about 200 cm. The apparatus has been described in detail previously.[7,8]

The principle of the flight-time-difference method applied to the H-H_2 fragmentation of H_3 is explained briefly by means of Fig. 1. The velocity of the center of mass (c.m.) of the projectile changes only slightly during the collision. Because of the fragment-mass ratio, the detectors were set at angles $\theta_1 = 2\theta_2$ with respect to the beam direction. The coincidence rate drops quickly when one angle deviates by more than 0.1° from this relation. This shows that threefold fragmentations do not need to be taken into account. The flight-time difference spectrum taken at this angle records all events whose components of $\vec{v}$ perpen-

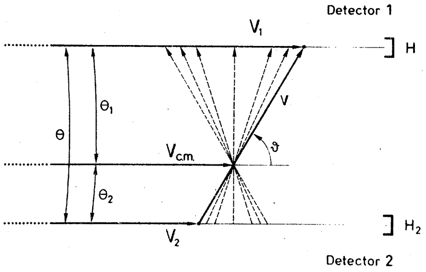

FIG. 1. Kinematic diagram of the H-H_2 fragmentation of fast H_3. $\vec{V}_{c.m.}$, $\vec{V}_1$, and $\vec{V}_2$ are velocities in the laboratory frame of the c.m. of H_3, the H fragment, and the H_2 fragment, respectively. The common origin of $\vec{V}_{c.m.}$, $\vec{V}_1$, and $\vec{V}_2$ is far to the left. $\vec{v}$ is the fragment velocity in the c.m. frame. θ_1 and θ_2 are the scattering angles in the laboratory frame.

dicular to the beam direction are $\theta V_{c.m.}$, where $\theta = \theta_1 + \theta_2$. Some of them are shown in Fig. 1. The length of the $\vec{v}$ vectors shown in Fig. 1 was chosen such that they differ from one another by a constant amount. The largest change in velocities in the laboratory frame obviously occurs for orientations of $\vec{v}$ about the perpendicular to the beam direction. This means that for a given time resolution, the best velocity or energy resolution in the c.m. frame is achieved for orientations of $\vec{v}$ near $\vartheta = 90°$. Then, however, a good angular resolution is required. The width of the detector entrance slits was 0.4 mm, thus limiting the angle of acceptance to 0.01°.

The smallest velocity in the c.m. frame that can be recorded at a given angle θ is that with $\vartheta = 90°$. If smaller velocities are to be measured, the angle θ has to be decreased. If larger velocities are to measure with better resolution, the angle θ must be increased. To cover the range of interest, 11 different angles were chosen. Figure 1 shows that each velocity v which appears in the forward direction appears once more in the backward direction. The appearance of symmetrically located peaks in the flight-time-difference spectra serves as an aid in determining the origin of the spectra. The right- and left-hand side of the spectra were then added in order to improve the statistics. Flight-time-differences were converted into translational energies of both fragments in the c.m. frame, i.e., $\epsilon = \frac{1}{3} m v^2$ (m is the proton mass).

III. RESULTS

Figure 2 shows the results. The energy distributions give the number of H-H_2 fragmentations within the solid angle element $d\omega$ with respect to the c.m. of the H_3^+ ion when an energy between ϵ and $\epsilon + d\epsilon$ is released as kinetic energy of both fragments in the c.m. frame. The plots cover the energy range in which the step mentioned in the preceding paper[1] appears. There is, indeed, a rich structure of peaks in this energy range. The structure disappears when the H_3^+ ions are produced at low pressure in the ion source (~0.05 mbar). On the other hand, the structure does not change when the pressure is increased further.

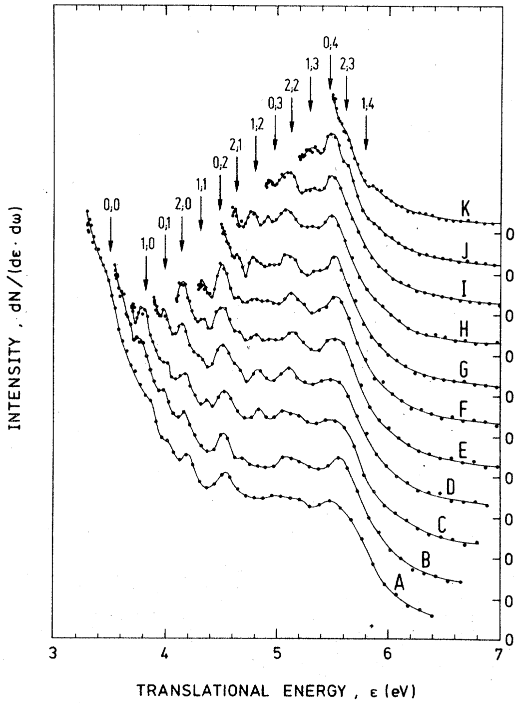

FIG. 2. Center-of-mass frame energy distributions of H-H_2 fragment pairs arising from dissociative electron-capture collisions of vibrationally deexcited H_3^+ at 10 keV. Target gas is H_2. The angles θ of observation (see Fig. 1) are 2.21° (curve A), 2.29° (B), 2.34° (C), 2.40° (D), 2.46° (E), 2.52 (F), 2.58° (G), 2.61° (H), 2.69° (I), 2.77° (J), 2.85° (K). The numbers on top of the peaks are explained in Sec. IV.

Each plot begins with $\vartheta = 90°$. Here the flight-time difference is zero, and the energy resolution is highest. The strong peaks appear in all curves when the relevant energy range is covered. The weak peaks appear mainly at the beginning of the curves, where the energy resolution is high. Since ϑ changes with ϵ (compare Fig. 1), the curves plotted in Fig. 2 could also be represented as angle distributions, as well as energy distributions. A comparison of the curves, however, shows that the peaks always appear at the same energies. Furthermore, the intensity ratio of adjacent peaks is the same in different plots. This shows that there is little anisotropy in the intensity distribution.

The linearity of the energy scale is better than

±0.02 eV; the absolute position of the whole energy scale is estimated to be accurate within ±0.04 eV. The number of counts is approximately 5000 in the 5.5-eV peak for each curve. Thus the statistical error is smaller than 2%. The accumulation time for each curve was about 48 h.

IV. DISCUSSION

Peaks of appropriate energies and spacings in the translational-energy spectrum can be expected when vibrational levels of a bound excited state of H_3 are predissociated by another electronic state with a lower dissociation limit. If we assume that the H and H_2 fragments are formed in their electronic ground states, then the lower state is the electronic ground state of H_3. The electronic ground state is a doubly degenerate state of species $^2E'$ in the equilateral D_{3h} conformation.[9] It exhibits the Jahn-Teller effect.[10] The degeneracy is removed by forming an upper and lower potential-energy sheet with a conical intersection for non totally symmetric displacements of the nuclei. The upper sheet represents a quasibound excited state which has a potential minimum for an equilateral-triangle configuration with sides of 1.965 a.u. (the H_3 minimum in D_{3h} conformation).[4] It lies 2.875 eV above the $H+H_2$ minimum,[4] or 2.60 eV above $H+H_2$ in its ground vibrational state.

TABLE I. Energies and populations of vibrational levels in the upper Jahn-Teller sheet of H_3 produced by electron capture of H_3^+ (in its ground vibrational and first excited E levels).[a]

1 $H_3^+ \rightarrow H_3$ A E A E No. of quanta	2 Franck-Condon factor	3 Level population[b]	4 Energy	5 Energy in eV[c] d	6 e	7 Observed levels in eV
0 0 0 0	a	a	0	3.59	3.50	
0 0 1 0	b	b	e_A	3.85	3.82	3.80
0 1 0 1	d	dx	e_E	4.01	3.99	3.99
0 0 2 0	c	c	$2e_A$	4.11	4.14	4.16
0 1 1 1	$\frac{b}{a}d$	$\frac{b}{a}dx$	e_A+e_E	4.27	4.31	4.33
0 0 0 2	e	e	$2e_E$	4.43	4.48	4.50
0 1 2 1	$\frac{c}{a}d$	$\frac{c}{a}dx$	$2e_A+e_E$	4.53	4.63	4.62
0 0 1 2	$\frac{b}{a}e$	$\frac{b}{a}e$	e_A+2e_E	4.69	4.80	4.79
0 1 0 3	f	fx	$3e_E$	4.85	4.97	4.93
0 0 2 2	$\frac{c}{a}e$	$\frac{c}{a}e$	$2e_A+2e_E$	4.95	5.12	5.10
0 1 1 3	$\frac{b}{a}f$	$\frac{b}{a}fx$	e_A+3e_E	5.11	5.29	5.30
0 0 0 4	g	g	$4e_E$	5.27	5.46	5.48
0 1 2 3	$\frac{c}{a}f$	$\frac{c}{a}fx$	$2e_A+3e_E$	5.37	5.61	5.62
0 0 1 4	$\frac{b}{a}g$	$\frac{b}{a}g$	e_A+4e_E	5.53	5.78	5.85
0 1 0 5	h	hx	$5e_E$	5.69	5.95	
0 0 2 4	$\frac{c}{a}g$	$\frac{c}{a}g$	$2e_A+4e_E$	5.79	6.10	

[a] Columns 1–4 are given by Porter (Ref. 4).

[b] Assuming relative population x for excited H_3^+ (1 quantum in E mode).

[c] With respect to $H+H_2$ in its ground vibrational level.

[d] With $e_A=0.26$ eV, $e_E=0.42$ eV, and the energy of the ground vibrational level of 3.59 eV (Ref. 4).

[e] With $e_A=0.32$ eV, $e_E=0.49$ eV, and the energy of the ground vibrational level of 3.50 eV (this work).

Sections through the upper Jahn-Teller sheet along the three normal-mode coordinate axes about the potential minimum are shown in a paper by Porter *et al*.[11] The totally symmetric breathing vibration has a dissociation limit of 4.48 eV above $H + H_2$ in its ground vibrational state (the potential energy of three H atoms for infinite separations). The degenerate vibration has a potential barrier of 5.92 eV above $H + H_2$ in its ground vibrational state.[11]

Porter[4] has calculated the energies of vibrational levels in the upper Jahn-Teller sheet and has estimated the relative populations of the levels which may be encountered in this experiment. They are given in Table I. His results can be summarized as follows: The H_3^+ ions are assumed to be in their ground vibrational state with weight 1, and in their first excited E vibration with weight x. The E excitation is necessary if odd quanta are to be excited in the H_3 upper sheet, since the Franck-Condon overlap is zero for even → odd transitions in the absence of the perturbation by the captured electron. Since little is known about this perturbation, it is difficult to give the populations quantitatively. Therefore, the Franck-Condon overlaps are left as free parameters. Since the H_3 minimum is at $R \sim 1.965$ a.u., and the H_3^+ minimum at $R \sim 1.65$ a.u., the excitation of a few quanta of the A breathing mode in H_3 is to be expected. The zero-point energy for vibrations in the upper Jahn-Teller sheet is about 0.97 eV. This quantity is, however, probably somewhat overestimated. Thus the ground vibrational state of excited H_3 lies about 3.59 eV above $H + H_2$ in its ground vibrational state. The H_3 vibrational quanta in the upper sheet are approximately $e_A = 0.26$ eV and $e_E = 0.42$ eV for the breathing and degenerate vibrations, respectively. These may well be overestimates, as they do not take into account normal-mode interactions.

The energy levels calculated on the basis of Porter's values for vibrational quanta and zero-point energy are given in column 5 of Table I. The observed energy levels are given in column 7. The calculated energies appear in the same general energy range as that of the observed levels. Moreover, the estimated level populations correctly reflect the experimental result of alternating strong and weak peaks (see Fig. 2), if one assumes that the first E vibration in H_3^+ is excited somewhat weaker than the ground vibrational state (i.e., $x < 1$). The agreement between calculated and observed energies is, however, not satisfactory, especially for the higher levels.

We tried to achieve a better agreement with experiment by using modified values for vibrational quanta and zero-point energy. The ground vibrational level was assumed to lie 3.50 eV above $H + H_2$ in its ground vibrational state. This means that the zero-point energy would be 0.88 eV instead of 0.97 eV. The H_3 vibrational quanta were assumed to be $e_A = 0.32$ and $e_E = 0.49$ eV for the breathing and degenerate vibrations, respectively. The levels derived from these values are given in column 6 of Table I. They are also indicated by arrows in Fig. 2. The first number above an arrow gives the number of quanta excited in the breathing mode, and the second number stands for the number of quanta excited in the degenerate bending mode. For this set of energy parameters there is excellent agreement between predicted and observed peaks with respect to both positions and intensities with the following two exceptions: The ground vibrational level at 3.50 eV seems to be missing, and the last observed peak at 5.85 eV is too high to be attributed to $e_A + 4e_E$.

At the estimated position of the missing ground vibrational level a very weak, but broad, hump appears. A possible explanation is a broadening of the ground vibrational level due to a very short lifetime with respect to predissociation (of the order of 10^{-14} sec). A shorter lifetime is not surprising, since the ground vibrational level is closest to the point of conical intersection of the two potential surfaces.

A remarkable feature of Fig. 2 is the sudden decrease of intensity above 5.5 eV. This energy is not far away from the height of the potential barrier of about 5.9 eV which appears in the degenerate vibration. The limit, above which vibrational structure disappears, might even be lower if tunneling through this barrier or predissociation by vibration[12] into the dissociation continuum of the breathing vibration is taken into account. In the light of this, it is not surprising that the last resolved peak at 5.85 eV does not fit very well into the general scheme.

As has already been discussed above, the observed energy levels reflect the predicted intensity alternation of stronger and weaker levels. This, however, implies that a not negligible fraction of H_3^+ ions is in its first E vibration. In order to find out if the vibrational temperature of the H_3^+ ions can be decreased further by increasing the hydrogen pressure in the ion source, the pressure was raised, by a factor of 3, to about 3 mbar. The spectrum, however, remained unchanged. Thus the assumption that the H_3^+ ions are essentially in their ground vibrational state, if the ion-source pressure is sufficiently high, is in contrast to the result of this experiment.

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[1] M. Vogler and B. Meierjohann, J. Chem. Phys. 69, 2450 (1978).

[2] M. Vogler and B. Meierjohann, Phys. Rev. Lett. 38, 57 (1977).

[3] B. Meierjohann and M. Vogler, Phys. Rev. A 17, 47 (1978).

[4] R. N. Porter (private communication).

[5] J. J. Leventhal and L. Friedmann, J. Chem. Phys. 50, 2928 (1969).

[6] B. Peart and K. T. Dolder, J. Phys. B 7, 1567 (1974).

[7] B. Meierjohann and M. Vogler, J. Phys. B 9, 1801 (1976).

[8] B. Meierjohann and M. Vogler, Z. Phys. A 282, 7 (1977).

[9] G. Herzberg and H. C. Longuet-Higgins, Discuss. Faraday Soc. 35, 77 (1963).

[10] H. A. Jahn and E. Teller, Proc. R. Soc. Lond. A 161, 220 (1937).

[11] R. N. Porter, R. M. Stevens, and M. Karplus, J. Chem. Phys. 49, 5163 (1968).

[12] See G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, Princeton, N.J., 1966), p. 458.