

A NEW TEST OF TRANSLATIONAL SPECTROSCOPY: THE ROTATIONAL PREDISSOCIATION OF THE $X^1\Sigma$ STATE OF HeH^+

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Abstract

We have repeated the experiment on the accurate measurement of the kinetic energy released during the predissociation of HeH^+ ions into the fragments H^+ and He. This experiment was carried out on two machines specially designed for this purpose. The new results differ from those of the original experiment and agree now very well with the theoretical predictions.

I. INTRODUCTION

Predissociation of molecular ions mainly has been investigated indirectly by studying line broadening and intensity distributions of emission and absorption lines. As the discrete internal energy of the metastable levels above the dissociation limit is released as kinetic energy of the fragments, a study of the fragment kinetic energy distributions can establish a new spectroscopy of these predissociating states. The energies involved are too low (10^{-5} eV until a few eV), to be measured directly. Moreover the initial thermal energy distribution of the parent ions obscures the measurements. However, in fast ion beams, using either an electrostatic or a magnetic analyser the measurements of these low kinetic energy distributions can be performed very accurately.

In 1969 Schopman and Los [1] using a mass spectrometer, observed a well-resolved fine structure in the proton peak which was due to the dissociative process $\text{HeH}^+ \rightarrow \text{He} + \text{H}^+$. These structures showed up in the spontaneous and, even more rich, in the collision induced proton fragment spectra. This discovery stimulated the use of translational spectroscopy in studying non-radiative decay processes of excited molecular ions. Several research groups did study predissociation of molecular ions in this way, for example N_2^+ [2-5], NO^+ [6,7] and also the rotational predissociation of H_2^+ [8] and He_2^+ [9]. The same technique was applied to the photodissociation of H_2^+ in a fast beam experiment enabling to identify the individual vibronic transitions from $\text{H}_2^+(1s\sigma_g, v)$ towards the $\text{H}_2^+(2p\sigma_u)$ state, due to photon absorption [10,11].

An extensive review of this technique was published in refs. [12,13]. However, a rigorous test on the reliability and accuracy of the new spectroscopy has not yet been performed.

Apart from the fact that one needs then highly accurate measurements corrected for apparatus effects if necessary, one must have precise ab initio results. Both conditions are at this moment fulfilled in the case of HeH^+ . Firstly because the HeH^+ ion is relatively simple and it has been frequently the subject of theoretical studies. Secondly the experimental momentum distribution of forward and backward scattered H^+ fragments shows exceptionally well spaced peaks at residual gas pressure ($< 10^{-7}$ torr).

The explanation of these spectra aroused much discussion [14,15], and it was Peek [16] who gave the explanation in terms of a rotational predissociation mechanism and sustained this with direct evidence. He calculated the energies and energy widths of all possible quasi-bound vibrational rotational levels of the ground state of $^4\text{HeH}^+$, $^4\text{HeD}^+$, $^3\text{HeH}^+$ and $^3\text{HeD}^+$, using the potential curves of Helbig et al. [17] and of Green and Michels [18]. Accepting a lifetime window compatible with the experiments, the agreement between theory and

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experiment, for each isotope, was close enough to confirm this explanation.

The slight discrepancies inspired both theoreticians and experimentalists to improve their accuracy [19]. The calculations were redone recently by Kołos and Peek [20] and we will describe here the new experimental data simultaneously obtained by the Amsterdam and by the Orsay research groups. The two machines were different in concept but both specially designed to measure accurately the kinetic energy distributions of dissociative fragments.

2. EXPERIMENTAL PROCEDURES

In both experiments the kinetic energies of the fragments is measured in a frame which has a high velocity with respect to the frame of the center of mass of the molecular ion. Then the spread in the measurements due to the thermal energy distribution of the primary molecular ions is made negligible. For a careful analysis the reader is referred to the reviews given in refs. [12,13].

In the two machines an ion beam of vibrationally and rotationally excited HeH^+ is directed through an interaction chamber. A voltage is applied to the chambers which shifts the energy distribution of the charged fragments originating in this region with respect to the background spectrum, caused by unimolecular dissociations in other parts of the apparatus. Moreover, a strong collimation is applied both in front and after the chamber in order to accept only those fragments which dissociate in the beam direction. Then the analyser will measure the forward-backward momentum distribution of the fragments only.

Accurate energy measurements require a very good alignment, an angular resolution compatible with the energy resolution and of course a high resolving power of the analyser [12,13]. For the experiments reported here, performed at accelerating voltages of 5 keV to 15 keV a resolution of 1:3000 was necessary.

We will now briefly describe the two machines.

2.1. Orsay apparatus

The ion beam is ejected by a Colutron Ion Gun operating in the monoplasmatron mode. The ion source was modified to improve the pumping and the cooling of the anode. The energy spread of this set up was 0.2 eV for an extraction voltage of 5000 V. After focusing the ions are preanalysed by a Wien filter. The angular definition of incoming and scattered ion beams is about 5×10^{-4} rad, using collimating holes between 40 and 80 μ . Deflection plates were built in to correct for the earth magnetic field. Having passed an interaction chamber with a length of 10 cm, the energy of the ions is analysed by a 127° electrostatic analyser (20 cm radius). The selected fragments are counted and stored in a multichannel analyser which drives the electrostatic analyser. Further details are given in ref. [12].

2.2. Amsterdam apparatus

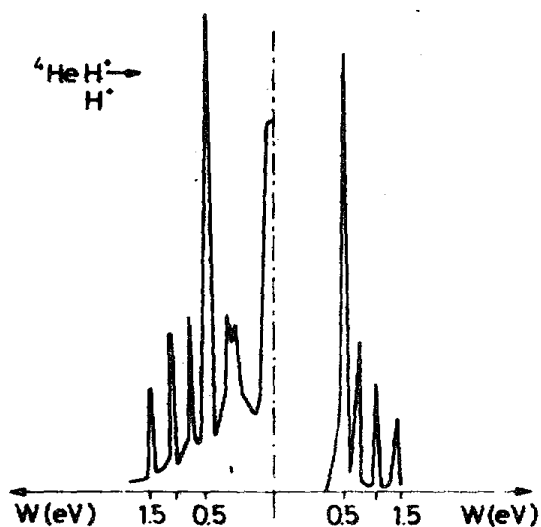
This machine is essentially a tandem mass spectrometer of which an extensive description is given in ref. [8]. From a monoplasmatron ions are extracted and accelerated to 10 keV or 15 keV, focused and then preselected by a first magnet. The collimation of the primary and secondary ion beams is here $\approx 10^{-3}$ rad. The interaction chamber is interchangeable and had a length of 17.5 cm in this experiment. The fragments are momentum analysed by a high resolution mass spectrometer operating with an inhomogeneous magnetic field [8]. The fragments are counted and this signal is connected via a ratemeter to the y-axis of an x-y recorder. The x-axis is driven by the scanning mass spectrometer.

3. RESULTS

The HeH^+ is formed in the sources by an ion-molecule reaction [1, 14] ; following Schopman [1] both experiments were performed using a mixture of 90% He and 10% H_2 as a source gas, at pressures in the range of 10^{-1} to 10^{-2} torr. In fig. 1 a typical result of the French apparatus is shown, putting the interaction chamber at 100 V. The left hand side of the spectrum shows the backward side of a full distribution, taken at residual gas pressure. Because the background pressure in the chamber ($\approx 10^{-5}$ torr) is not low enough and secondly, the flight time to the localisation chamber is rather long, the collision induced contribution dominates the central part of the spectrum. This contribution was subtracted in the following manner. First 100 scans at background pressure were accumulated. Then 1 scan at 10^{-3} torr with air as target gas was carried out and subtracted from the accumulated spectrum. As all scan periods were kept equal, the remaining spectrum contained the

predissociation contribution only, which showed 4 peaks. This result is presented in the right hand side of fig. 1.

Fig. 1. Proton momentum distribution measured in Orsay. The left part is taken at background pressure, the right side shows the spectrum corrected for collision induced dissociation. The scale indicates the total center of mass energy released during dissociation.



In fig. 2 an example of an Amsterdam momentum scan is presented. The voltage of the chamber here was -200 V and the residual pressure could be kept at 2×10^{-8} torr. Therefore the background signal is negligible. An interesting feature is the small extra peak at low κ -value (center of mass momentum). This peak is absent in

Fig. 2. Forward-backward proton momentum distribution measured in Amsterdam. Here the scale indicates the momentum of proton in the center of mass (not corrected for convolution effects). The backward flying fragments show up in the left side of the figure.

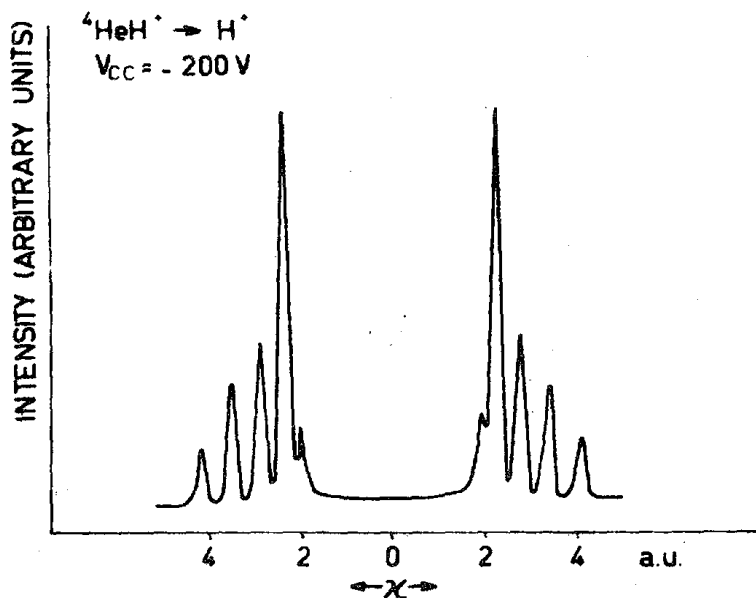


fig. 1, while in the experiment of Schopman this peak dominated the whole spectrum [1,15]. Now the flight time t_0 for the ions to reach the interaction chamber varies drastically for the 3 experiments: in the apparatus of Schopman, $t_0 = 0.6 \times 10^{-6}$ s, for the Orsay apparatus, we have $t_0 \approx 2.6 \times 10^{-6}$ s and in Amsterdam $t_0 \approx 1.4 \times 10^{-6}$ s. This suggests strongly that the lifetime of this specific level is significantly shorter than for the other observed states. It will be in the order of 10^{-6} s, which is in agreement with the observations of Schopman [15], Houver et al. [14] and Peek [16].

Experiments are in progress to establish a more accurate determination of the lifetimes involved [21].

After careful calibrations and an analysis of the apparatus effects, the energies in the center of mass system could be calculated. With regard to the Orsay data, it was shown by Comtet [22] that the apparatus function did not affect the energy measurements for the given energy and angular resolution of the machine.

However, the Amsterdam measurements are distorted by the apparatus function and to eliminate this, computer simulations of the experiment were carried out [8]. The resulting figures are listed in table 1 and compared with the earlier data of Schopman. The theoretical results of Peek [16], together with an assignment of vibrational and rotational quantum numbers are also indicated. The last two columns show the most recent theoretical data of Kolos and Peek [20].

4. CONCLUSIONS

A first conclusion is that the results of the two experimental groups agree very well, although the two machines are different in design. This proves the reliability of this technique for measuring discrete kinetic energies of dissociating fragments in the molecular center of mass coordinate system. The discrepancy of some 20% between our data and the data of Schopman is probably due to apparatus effects, for which he should have corrected. He used an interaction chamber at 140 V, which as we know now, decreased the energy scale by $\approx 8\%$. Moreover, this apparatus was not designed to measure phenomena occurring at $0^\circ \pm 10^{-4}$ rad with respect to the beam direction. As a non-zero angle especially will affect the measurement of the lower e_d values, larger discrepancies are likely to occur here.

Now, the agreement between the experimental energy values and both sets of theoretical values is very satisfactory and proves the high quality of the potential curves used. Considering the error bars, however, we cannot distinguish between the two calculations. As the calculated energy widths (inverse lifetimes) apparently are much more sensitive to the used potential, experimental data on the lifetimes are needed to discriminate between the two theories [21].

Table 1-Comparison between experimental and theoretical energy values (e_d): $e_d(1)$ = Orsay data; $e_d(2)$ = Amsterdam data. Γ stands for the calculated energy widths of the levels, v, J = vibrational and rotational quantum numbers. All data in atomic units

$10^3 e_d$ [15]	$10^3 e_d(1)$	$10^3 e_d(2)$	$10 e_{dth}$ [16]	$10^{12} \Gamma$ [16]	v	J	$10^3 d_{th}$ [20]	$10^{12} \Gamma$ [20]
4.96 ± 0.1	5.48 ± 0.16	5.44 ± 0.16	5.44	1.8	0	25	5.39	1.5
3.40 ± 0.09	3.79 ± 0.12	3.79 ± 0.12	3.78	2.5	1	23	3.71	1.7
2.31 ± 0.05	2.50 ± 0.09	2.54 ± 0.09	2.57	3.3	2	21	2.50	1.8
1.52 ± 0.04	1.72 ± 0.09	1.76 ± 0.09	1.76	8.8	3	19	1.69	4.2
$1.05^a)$	-	1.25 ± 0.06	1.25	92	4	17	1.20	45

^{a)} The positions of the maxima were normalized with respect to this peak.

Acknowledgement

This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research on Matter) and was made possible by financial support from the Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research). The work performed at Orsay was made possible by contract ATP No. 1105 with the C.N.R.S.

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