Published in : Chemical Physics (1976), vol. 15, pp. 179-184
Status: Postprint (Author's version)

THE ROTATIONAL PREDISSOCIATION OF HeH$^+$: ENERGY AND LIFETIME MEASUREMENTS

R. LOCHT[1], J.G. MAAS, N.P.F.B. VAN ASSELT and J. LOS

FOM-Instituut voor A loom- en Molecuulfysica, Kruislaan 407, Amsterdam

Abstract

Relative lifetimes and energies above the dissociation limit have been determined for the rotational predissociation of several quasibound levels of the $X^1\Sigma^+$ state of ^{4}HeH$^+$. In particular the lifetimes are very sensitive to the shape of the potential energy curve. These measurements are used to discriminate between two ab initio potential curves, which differ by only 0.00004 au (≈ 1 meV). Using the lifetime data, relative population factors were determined for the observed levels.

1. Introduction

The spontaneous dissociation of 10 keV HeH$^+$ ions into He and H$^+$ has been investigated first by Schopman et al. [1,2]. This work was extended to isotopically labeled molecular ions [3]. The proton momentum distribution spectra showed 5 discrete peaks. It was suggested by Schopman et al. [1], as well as by Hbuver et al. [4] that these discrete peaks were due to rotational predissociation (i.e., tunneling through a rotational barrier) of the molecular ion. Finally Peek [5] provided a profound basis for this explanation. This author calculated the energies and energy widths of all possible metastable vibrational-rotational levels of HeH$^+$ and its isotopes. Taking into account the experi-ψ mentally accepted lifetime range, a very reasonable correspondence between theory and experiment was found. Recently, Kolos and Peek [6] reinvestigated the potential energy curve of HeH$^+$ and calculated again the energies and widths of the levels.

The new energy values did not differ much from the former work. Consequently the discrepancies between theory and experiment remained in the same order of magnitude, which suggested now the occurrence of an error in the experiment. To check this, new experiments were performed by a French group and by this group independently [7]. This time the influence of apparatus effects was accounted for by introducing a simulation of the experiments with the computer. Now good agreement is found between theory and experiment. Secondly, as a comparison between the two calculations demonstrates that the energy widths are much more sensitive to the shape of the potential than the energies [6], measurements were performed to determine relative lifetimes of the observed levels. The present experiment clearly shows that the potential curve of Kolos and Peek does predict the lifetimes much better.

2. Experimental

2.1. Apparatus

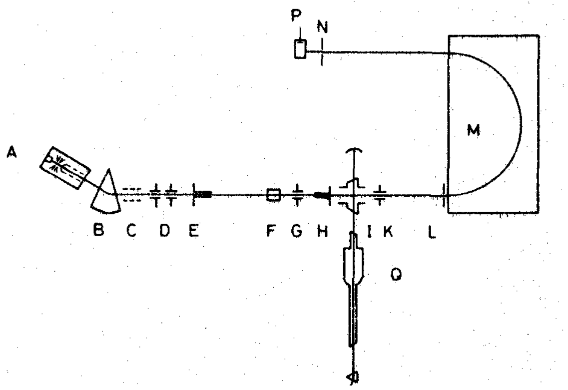
The experimental set-up (see fig. 1) used in this work has been described previously in detail [8]. Briefly, HeH$^+$ ions are created in a monoplasmatron ion source (A). The energy spread of the ion beam is reduced by monitoring and keeping constant (i) the gas flow of the 90% He-10% H_2 gas mixture, and (ii) the plasma oscillations which are maintained as low as possible. The primary ion beam is mass-selected by a 30° preselection magnet (B). Lenses (C), deflection plates (D) and collimator (E) focus the ion beam on the entrance hole of a 17.5 cm long collision chamber (F), in which a target gas can be introduced. The ion path length between the source exit and the center of the collision chamber is 110 cm. By means of the plates G and K the ion beam is directed on a 0.25 cm hole L. The energy excess of some quasi-stable vibrational-rotational level above the dissociation limit will be released as kinetic energy of the two dissociating fragments. The hole L is used to skim off the larger angles in the center-of-mass system, permitting only a recording of the forward-backward momentum distribution by the scanning magnet M. This inhomogeneous magnet focusses the ions on a narrow (0.03 cm) slit (N), before reaching a Bendix electron multiplier. A laser (Q), not used in these experiments [9], crosses the ion beam in a 3 cm long chamber (I), at 160 cm from the aperture of the ion source. To either the collision chamber or the laser chamber a voltage can be applied (see section 2.2.1). In this series of experiments an ion extraction voltage of 10.6 kV is used whereas 10.6 kV and 15.8 kV accelerating voltages are applied to the ion beam. Negative voltages of respectively 200 V and 300 V are applied to the collision chamber

---

[1] On leave from Institut de Chimie, Sart-Tilman par B 4000 Liège 1, Belgium.

and the laser chamber. The working pressure in the primary selection region is 3 X 10^{-6} torr. In the interaction region F a pressure of 3 X 10^{-8} torr and in the momentum analyzing region a pressure of 3 X 10^{-9} torr is measured under normal operating conditions.

Fig. 1. *Schematic outline ot" the apparatus. Details are explained in the text.*



2.2. Principle of measurements

2-2.1. Lifetime measurements

The relative lifetime measurements are made possible with the instrument just described, by changing the flight time of the ionized species. This can be achieved by (i) altering the accelerating high voltage, and/or (ii) changing the position of the interaction chamber where metastable decomposition is observed. The procedure consisting by applying a voltage to either the collision or laser chamber allows to separate the fragment momentum distribution spectrum observed in the interaction chamber in question from those resulting from dissociations occurring along the whole ion beam path between the preselection magnet and the momentum analysers entrance hole [2,8].

As shown by Maas et al. [8]. the number of metastable ionsJ_0 with lifetime τ, decaying per unit time within one of the interaction chambers is given by

$$J_0 = 2I_0 \exp(-t_0/\tau)\sinh[\Delta t/(2\tau)] , \qquad (1)$$

where I_0 is the partial primary beam intensity of metastable ions characterized by lifetime r, leaving the ion source; Δt is the flight time to pass through the interaction chamber and t_0 is the flight time to reach the center of the interaction chamber.

In the following discussion subscripts *i*c and *i*l will be used for metastable level *i* observed in the collision chamber and in the laser chamber respectively.

When the intensity corresponding to level *i* is normalized to the intensity of level *j* as observed in the same interaction chamber, the ratio J_i is related to τ_i and τ_j by

$$J_i = (I_{0i}/I_{0j})(\tau_j/\tau_i)\exp[-t_0(1/\tau_i - 1/\tau_j)] \qquad \mathbf{(2)}$$

using the approximation sinh $[\Delta t/(2\tau)] \approx \Delta\tau/(2\tau)$.

The ratios J_{ic} and J_{il} were obtained by recording the momentum distribution spectra alternatively from either the collision chamber or the laser chamber, keeping the ion source conditions constant. Then the ratio of J_{ic} and J_{il} is given by

$$J_{ic}/J_{i1} = \exp[-(t_{0c}-t_{01})(1/\tau_i-1/\tau_j)]$$
$$= \exp[-(t_{0c}-t_{01})(\Gamma_i-\Gamma_j)] \quad \textbf{(3)}$$

where $\Gamma = 1/\tau$ represents the energy width of the level.

The same ratio is valid for 10.6 kV and 15.8 kV accelerating potentials, differing by the t_{0c} and the t_{0c1}values only. For those levels observed for two acceleration potentials in the same chamber, the same type pf equation as (3) holds, i.e.,

$$J_i^{10\,\mathrm{kV}}/J_i^{15\,\mathrm{kV}} = \exp[-(t_0^{10\,\mathrm{kV}}-t_0^{15\,\mathrm{kV}})(\Gamma_i-\Gamma_j)] \quad (3')$$

providing the population factor ratio I_{0i}/I_{0j} is constant in both experimental conditions. This assumption is reasonable because we maintained the ion extraction voltage at 10.6 kV and controlled the plasma conditions as well.

Moreover, the value of $(\Gamma_i$-$\Gamma_{j;}\cdot)$ thus determined in these experiments can be used in eq. (2) to calculate I_{0i}/I_{0j} which represents the relative population factor of level i upon leaving the ion source. The ratio τ_j/τ_i in eq. (2) then is calculated using a theoretical Γ_j value.

2.2.2. Energy measurements

As shown earlier by Maas et al. [8] the experimental data have to be corrected for the apparatus effects. A general treatment of this problem has been proposed by these authors and a computer simulation of the experiment has been developed. This procedure has been applied successfully to the case of the unimolecular dissociation of H_2^+ and D_2^+ [8] in order to obtain corrected e_d values (excess energy above the dissociation limit). The computer program has been changed in order to account better [8] for the ion-focussing properties of the chambers, so the shift and the change of scale (expanding) introduced by the negative voltages on the chambers are automatically been taken into account.

2.3. Data analysis

On the quantity to be measured, the lifetime τ_i resulting from the measurement of relative intensities, the major error source is the intensity measurement. The error in the flight time difference t_{0i}-t_{01} is negligible, being one order of magnitude smaller than the former. One has

$$\Delta(1/\tau_i-1/\tau_j) = \frac{\Delta(J_{ic}/J_{i1})}{(J_{ic}/J_{i1})(t_{0c}-t_{01})} \quad (4)$$

and

$$\frac{\Delta(J_{ic}/J_{i1})}{J_{ic}/J_{i1}} \approx \sum\left(\frac{\Delta J_{0i}}{J_{0i}}+\frac{\Delta J_{0j}}{J_{0j}}\right)_{c,1}, \quad (5)$$

the summation being extended over the measurements made in the two interaction chambers.

The magnitude of the ratio $\Delta J_{0i}/J_{0i}$, where ΔJ_{0i},· is given by the standard deviation of the mean, ranges from 1 - 3.5% and thus the value of $\Delta(J_{ic}/J_{il})/(J_{ic}/J_{il})$ is 2-7%. Using eq. (4) one calculates

$$\Delta(\Gamma_i\text{-}\Gamma_j) = (0.8 \text{ to } 3) \times 10^{-12}\ \mathrm{au},$$

which will be reduced averaging the data taken at 10.6 kV and 15.8 kV.

3. Results and discussion

Forward and backward momentum distribution spectra have been recorded for the fragment H^+, formed by dissociation of HeH^+ in the collision chamber and in the laser interaction chamber at residual gas pressure. These spectra are reproduced in figs. 2 and 3. They exhibit respectively five and four well resolved peaks.

As indicated in section 2.2.2, a computer simulation of the experiments was carried out to eliminate the influence of apparatus effects on the energy and lifetime measurements. By a recursive convolution method the energy values e_d above the dissociation limit were established which generate the observed apparent e_d values. One should compare only these "deconvoluted" e_d values with theory. To stress the importance of this procedure, the uncorrected as well as the corrected e_d values are listed in table 1, together with the theoretical values by Peek [5| and Kotos and Peek [6], taking into account a lifetime criterion as proposed by Schopman [3] and Maas [8].

***Fig. 2**. Example of a forward-backward momentum distribution of H^+ fragments from $^4HeH^+$, measured in the collision chamber, k stands for the ccnter-of-mass momentum of H^+ . The forward direction is on the right side. The voltage was V_{cc} = ---200 V.*

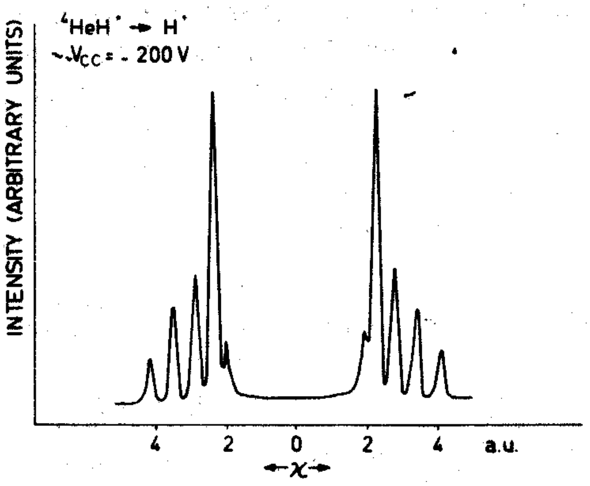
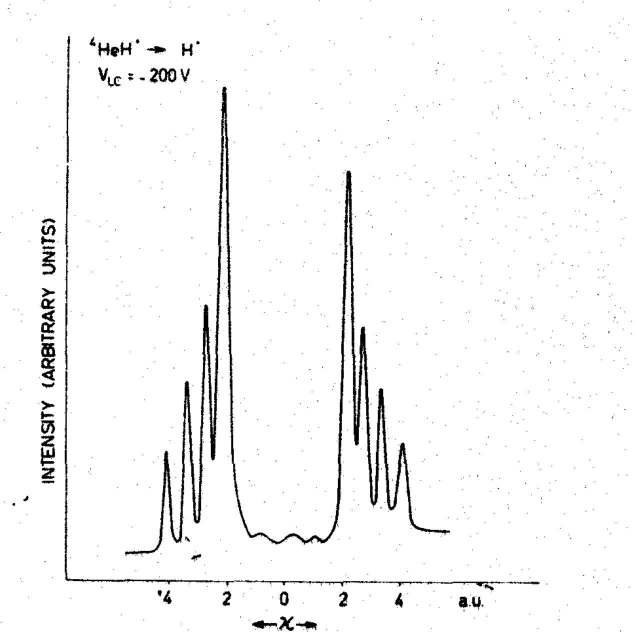


***Fig. 3**. Example of a momentum scan measured in the laser interaction chamber. See caption fig. 2.*



This criterion makes use of relation (1), First the lifetime τ is calculated at which J_0 is at maximum (J_{max})· This lifetime approaches t_0 if t_0 » Δt. Then it is accepted that only those levels will be observable for which τ,· yields a value of $J_0 \geq \alpha J_{\max}$. The choice of α is somewhat arbitrary: we have used α = 0.1. Taking either theoretical sets of Γ values, only 5 levels lay within the thus obtained window. Even by lowering the α-value with a factor 2, just the same levels obey the criterion.

Using the experimental data on e_d alone, it is difficult due to the experimental inaccuracies, to reject one of the two calculations. They lead to the same assignment of *υ* and *J,* the vibrational and rotational quantum numbers to the experimental peaks, together with only little different e_d values (see table 1). This is in agreement with the observations of Bernstein [10], Considering the measurements of Schopman, he used a Stwalley-Dunham fit to the experimental e_d values and proved the internal consistency of the assignments of the vibrational and rotational quantum numbers, as proposed by Peek. So only minor inaccuracies are expected to occur in the theoretical results.

However, theory should not only predict the correct energies e_d, but also the widths (or lifetimes) must be considered. The relative lifetimes are determined using the formalism developed in section 2.2.1. The intensity ratios J_i, corrected for apparatus effects and normalized with respect to the most intense peak 4 were determined as an average over 11 measurements. The energy widths differences Γ_i-Γ_4 deduced from these data at the two accelerating voltages, then were averaged and are presented in table 2. The errors indicated stand for the standard deviation of the mean. These results were first calculated using eq. (3), However, in the present experiment (at residual pressure) the peak corresponding to the lowest e_d value can be measured accurately only in the collision chamber at both accelerating voltages. So, to this particular peak 5, only eq. (3') could be applied. Now the time difference $t_{0c}^{10\text{kv}}$ - $t_{0c}^{15\text{kv}}$ difficult to establish, as a change in the lens voltage causes a change in retardation or acceleration of the ions. Therefore we calibrated this time difference by putting Γ_i-Γ_4 = -3.7 X 10^{-12} au, the average value obtained using eq. (3). These results also are presented in table 2. In the last columns the theoretical values calculated by Peek [5] and Kotos and Peek [6] as well as the quantum numbers (υ, *J)* corresponding to each observed level are listed.

From the comparison of the theoretical Γ values and the experiment we conclude that fairly good agreement is found within the experimental error limits for at least 3 experimental values of Γ_i-Γ_4 (1 through 3) and those predicted by Koit>s and Peek [6]. The deviation for Γ_5-Γ_4 may be caused by errors in the experiment as well as in the theory. The strong variation of this value from the first calculation to the second one suggests the occurrence of a large error bar here. Secondly, from an experimental point of view, peak 5 is rather small and close to peak 4 (see fig. 2). So, a relatively large systematic error caused by an overlap of intensities is possible, even when the computer simulations have small absolute errors.

Finally, we are now able to calculate the relative population factors I_{0i}/I_{04} using the Γ_4 value of Kotos and Peek in eq. (2). The experimental data presented in table 2 were used: for *i* = 1 through 3 we took the values from the first column, the value for *i* = 5 from the second. Due to the relatively large error bars in the data Γ_i-Γ_4, the estimated error in the calculated population factors amounts to a factor of 2. The results are listed in table 3. No calculations exist to our knowledge which predict population factors of these vibrationally and rotationally highly excited states.

Concluding, we remark that it is clear from tables 1 and 2 that the lifetimes are far more sensitive to the exact shape of the potential energy curve than the energy values e_d, especially considering the difference between the two potential energy curves, i.e., 0.00004 au [6].

The expression which gives the energy width Γ of a vibrational rotational state above the dissociation limit in the JWKB approximation (see, e.g., [11]) accounts for this effect: then Γ depends exponentially on the integrated (imaginary) momentum of the particle with mass μ (the reduced mass of the HeH^+ system) under the rotational barrier. This exponential amplifies small changes in the potential energy curve to distinctive changes in Γ.

So the mass-spectrometric study of dissociation fragments enabling relative lifetime measurements together with accurate energy determinations is a powerful technique, capable of sensing minimal potential energy differences (≈ 1 meV).

Table 1: *Comparison of measured and theoretical energy values. AH figures are rounded off to the second decimal place and are given in atomic units (1 au = 27.21 eV)*

Peak number	a) ^{e}d x10^{3}	b) ^{e}d corrx10^{3}	c) ^{e}d th x10^{3}	d) ^{e}d th x10^{3}	υ	J
1	5.84 ±0.16	5.44 ± 0.16	5.44	5.39	0	25
2	4.01 ±0.12	3.79 ±0.12	3.78	3.71	1	23
3	2.69 ± 0.09	2.54 ± 0.09	2.57	2.50	2	21
4	1.83 ±0.09	1.76 ±0,09	1.76	1.69	3	19
5	1.29 ±0.09	1.25 ±0.09	1.25	1.20	4	17

a) Apparent e_d values, direct from spectra.
b) Energies corrected for convolution effects.
c) Values calculated by Peek.
d) Values presented by Kolos and Peek, υ and J represent the vibrational and rotational quantum numbers assigned to the levels (identical for both calculations).

***Table 2**: Energy widths differences Γ_i-Γ_4 in atomic units*

1	(Γ_i-Γ_4)exp x 10^{12}		(Γ_i-Γ_4)th x 10^{12}		v	*J*
	a)	b)	[3]	[4]		
1	-3.7 ± 0.6	-3.-7 *	-7.0	-2.7	0	25
2	-3.3 ± 1.9	-2.1 ±1.3	-6.3	-2.5	1	23
3	-2.9 ± 0.7	-1.9 ±1.1	-5.5	-2.4	2	21
4	0	0	0	0	3	19
5	-	+11.6 ±4.7	+83	+41	4	17

a) Calculated using eq. (3).
b) Calculated using eq. (3'). *
Normalized, see text.

***Table 3** : Relative population factors fi determined from the experimental data on Γ_i-Γ_4 and the value Γ_4 = 2.4 X 10^{-12} au from [6]*

i	f$_i$
1	3.2
2	2.3
3	1.6
4	1.0*
5	0.1

* Normalized.

Acknowledgement

The assistance of Mr. P. Nowak and Mr. H.H. Holsboer is gratefully acknowledged.

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).

References

[1) J. Schopman. A.K. Barua and J. Los, Phys. Lett. 29A (1969) 112.

[2| (a) J. Schopman and J. Los, Physica 48 (1970) 190;

(b) J, Schopman and J. Los, Physica 51 (1971) 1

[3] J. Schopman, P.G. Ipurnier and J. Los, Physica 63 (1973) 518

[4] J.-C. Houver J. Baudon, M. Abignoli, M. Barat. P. Fournier and J. Durup, Internat. J. Mass Spectrom. Ion Phys. 4 (1970) 137.

[5] J. Peek, Physica 64 (1973) 93.

[6] W. Kolos and J. Peek, Chem. Phys. 12 (1976) 381.

[7| P.G. I Fournier, G. Comtet, R.W. Odom, R Locht. J.G. Maas, N.P.F ,B, van Asselt and J. Los, Chem. Phys. Lett. 40(1976) 170.

[8] JG. Maas, N.P.F .B. van Asselt and J. Los, Chem. Phys. 8(1975)37.

[9] N.P F. B. van Asselt. J.G. Maas and J. Los, Chem. Phys. 11(1975)253.

[10] R.B. Bernstein, Chem. Phys. Lett. 25 (1974) 1.

[11| R.J. LeRoy and RB. Bernstein, J. Chem. Phys. 54 (1971), 5114.