Dissociative Charge Exchange of HeH$^+$: An Experimental Study of the HeH Molecule

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(Received 5 May 1986)

We have studied the dissociation of HeH molecules produced in the charge exchange between fast HeH$^+$ ions and Cs. The released kinetic energy is measured by detection in a delayed coincidence technique of the neutral He-H pairs formed after dissociation. First direct evidence is reported for quasibound, predissociative states of HeH with energy levels in agreement with theoretical predictions. HeH* molecules are formed with large rotational and little vibrational excitation. The decay mechanisms of the low electronic excited states of HeH are discussed.

PACS numbers: 31.70.Hq, 33.80.Eh, 34.70.+e

From a theoretical point of view the HeH molecule is one of the simplest heteronuclear molecules, since its electronic properties can be explained by reference to basic ideas of quantum chemistry. Indeed, one expects a repulsive electronic ground state ($X^2\Sigma^+$) and attractive electronic excited states. These excited states belong to a Rydberg series that converges to the electronic ground state of the HeH$^+$ ion. The tight HeH$^+$ bond is due to charge-exchange interaction between the He+H$^+$ and He$^+$+H configurations along with some polarization effects of the He atom by H$^+$. These properties have been confirmed by molecular calculations performed on the HeH molecule.[1,2] Recent accurate *ab initio* results of Theodorakopoulos *et al.*[3] make possible now a precise determination of rovibronic levels of the low-lying excited states (especially the first two excited states: $A^2\Sigma^+$ and $B^2\Pi$). However, the decay mechanisms of these states by photoemission to and/or predissociation by the $X^2\Sigma^+$ ground state are still not known from theory since calculations of dipole transition moments and dynamic couplings are lacking.

From an experimental point of view little is known about the HeH molecule since the usual spectroscopic methods cannot be applied. The first pieces of information were provided by the field of atomic collisions. Among the abundant literature on collisions between hydrogen atoms and helium the experimental determination of the electronic excitations in this collision,[4] which focused on the effect of dynamical couplings, is of interest with respect to the present study. This effect was analyzed with reference to the Barat-Lichten molecular-orbital promotion model.[5] Very recently the existence of "bound" excited states of HeH was proved by emission spectroscopy of HeH* molecules produced in two ways: (i) by reactions of He and H$_2^*$,[6] and (ii) in charge-exchange collisions between HeH$^+$ and alkali vapors.[7] Still, these measurements do not lend themselves to a direct comparison with theory.

The present Letter shows the first direct evidence for predissociation of excited states of the HeH molecule and for the competition of predissociation and photoemission in this molecule. Moreover, the reported measurements provide the first experimental determination of the excited energy levels of HeH.

The experimental procedure has been described elsewhere,[8] therefore only a summary of the relevant details is reported here. The HeH$^+$ beam is formed in a Nier-type electron-impact source working at high pressure (0.1–1 Pa) with a 10:1 mixture of helium and hydrogen. After mass selection by a Wien filter the fast (6–10 keV) ion beam is directed through a collision cell (length = 0.8 mm) filled with cesium vapor. The target thickness is kept small in order to ensure single-collision conditions. Behind the collision cell all charged particles are deflected away. The neutral fragments resulting from the dissociative charge exchange process

$$\mathrm{HeH^+Cs} \to (\mathrm{HeH})^* + \mathrm{Cs}^+ \qquad (1)$$
$$\hookrightarrow \mathrm{He+H}$$

enter a field-free region of 580 mm length. Both fragments are detected in coincidence with a time- and position-sensitive detector. This device allows an accurate determination of the kinematics of the dissociation. Both the center-of-mass recoil angle (θ) with respect to the incident beam direction and the released kinetic energy (ϵ) are calculated on line and stored. Intrinsically the method has optimal resolution for equal-mass fragments. The present results concern the ^{3}HeD isotope. However, experiments have also been performed on ^{4}HeH and ^{4}HeD. For an absolute calibration of the dissociation energy scale we have replaced the HeH$^+$ beam by H_2^+ (D_2^+) and observed the structures associated with the predissociation of the $c^3\Pi_u^+$ state by the $b^3\Sigma_u^+$ state in H_2 (D_2).[8,9] The ac-

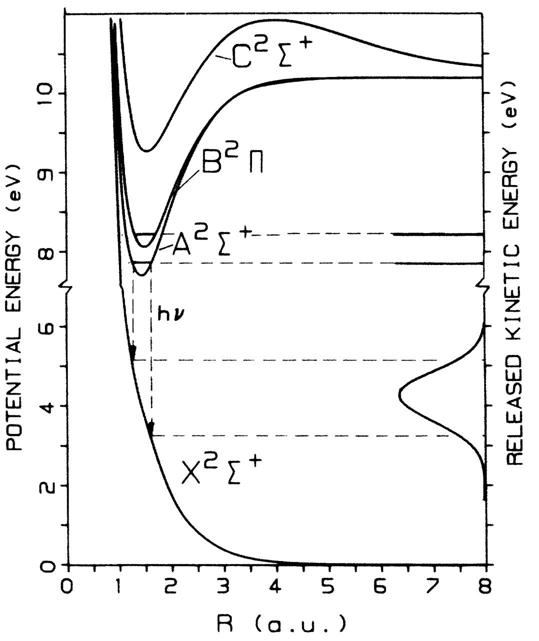

FIG. 1. Potential energy curves of HeH (from Ref. 3) and illustration of the decay mechanisms by photoemission (indicated by arrows) and by predissociation. A schematic spectrum of released kinetic energies is shown on the right side of the figure. The $HeH^+(v=0)+Cs$ channel lies at ≈ 7.8 eV.

curacy of the absolute scale is estimated to be 60 meV around $\epsilon = 8$ eV and the experimental resolution is better than 1%.

From comparison between the ionization potentials of Cs and the HeH molecule[2,3] at $R_e(HeH^+) = 1.46 a_0$ a predominant population at the $A^2\Sigma^+$ and $B^2\Pi$ states of HeH is expected (see Fig. 1; we follow the notation of Ref. 3). Populations of $X^2\Sigma^+$, $C^2\Sigma^+$, and higher excited states are less probable because of a larger energy defect in reaction (1). From the same arguments as those previously developed in the study of the dissociative charge exchange of H_2^+,[9] it is expected that the vibrational population of the Rydberg excited states of HeH closely reflects the vibrational population in the HeH^+ beam. The $A^2\Sigma^+$ and $B^2\Pi^+$ vibronic states can undergo decay by both photoemission to and predissociation by the $X^2\Sigma^+$ ground state. On the other hand, the $B^2\Pi^-$ component can only decay via photoemission. A schematic spectrum of released kinetic energies associated with the dissociation mechanisms of the A and B states is shown in Fig. 1.

According to the above discussion the continuous part, $\epsilon < 7.8$ eV, in the measured spectrum of Fig. 2 is due to radiative decay.[10] The structures observed for $7.8 < \epsilon < 10.5$ eV are due to *energy levels of predissociative states.* Further analysis of this part of the spectrum requires the knowledge of the rovibronic energy levels of the A and B states. The values of the lowest five vibrational levels of A and B states, calculated from available potential data,[3] are reported in Table I. This table shows that for each value of the vibration quantum number $v > 0$ the individual contributions of $A(v > 0)$ and $B(v-1)$ can hardly be distinguished experimentally.[11] Considering our energy resolution (better than 1%), the form of the peaks in Fig. 2 indicates *a broad distribution of rotational levels* in the HeH* molecules. The same conclusion was formed from the experiment of Ketterle, Figger, and Walther[7] where the HeH* molecules were produced in conditions very close to the present experiment. They proposed a rotational temperature of 3100 K. Experimentally, high-

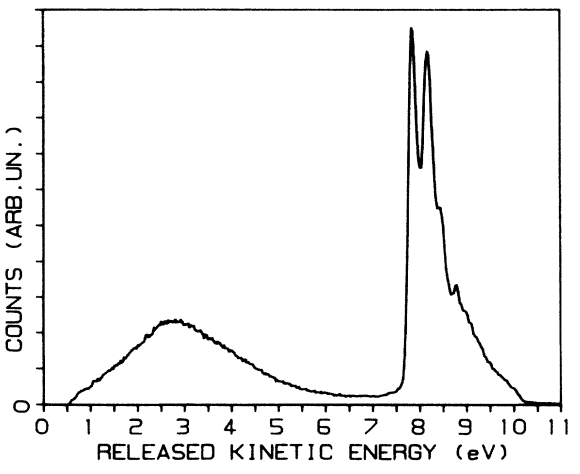

FIG. 2. Measured released kinetic energy spectrum at $\theta = 90°$ of ^3HeD molecules formed by a charge exchange between $^3HeD^+$ and Cs at 6 keV.

TABLE I. Lowest vibrational energy levels of the $A^2\Sigma^+$ and $B^2\Pi$ states of the ^3HeD molecule. The values are obtained by numerical integration of the Schrödinger equation with use of the potential data of Ref. 3. The energies are given with respect to the dissociation limit of the $X^2\Sigma^+$ ground state. For practical interest some spectroscopic constants are also reported.

Vibration quantum number	A state (eV)	B state (eV)
$v=0$	7.875	8.220
$v=1$	8.211	8.523
$v=2$	8.527	8.810
$v=3$	8.825	9.072
$v=4$	9.095	9.307
$v=5$	9.337	9.518
Spectroscopic values (cm^{-1})		
ω_e	2860	2630
$\omega_e x_e$	76	84

ly excited rotational levels have also been reported for the HeH^+ ions.[12]

In order to assign the peaks observed at energies between 7.8 and 10.5 eV, we have performed a computer simulation of the spectrum[13] using (i) rovibronic levels of the A and B states, calculated from the theoretical potential data,[3] (ii) a rotational temperature of 3100 K, independent of v, and (iii) the apparatus function. Only the sums of the populations of the $A(v>0)$ and $B(v-1)$ levels relative to that of the $A(v=0)$ level have been adjusted in order to fit the measured spectrum. The result of the simulation, shown in Fig. 3(a), *supports the calculated rovibronic levels,* although the experimental results suggest that the theoretical position of the A state (from Ref. 3) may be high by 40 ± 60 meV. From Fig. 3(a) we conclude that only the low vibrational levels ($v<3$) of HeH^* (and thus of HeH^+) are significantly populated. This finding is consistent with the results of calculations on the reactive collision[14] $\mathrm{H}_2^+ + \mathrm{He} \rightarrow \mathrm{HeH}^+ + \mathrm{H}$ for the vibrational distribution of the formed HeH^+ ions. The first peak in Fig. 3(a) is clearly due to *the predissociation of* $A(v=0)$. The other peaks can in principle consist of contributions from the predissociation of both $A(v>0)$ and $B(v-1)$. In order to estimate the relative importance of the A and B states two extreme hypotheses have been tested: (i) no predissociation of B, and (ii) maximal predissociation of the B state [i.e., the second peak in Fig. 3(a) is only due to predissociation of the B state]. From these two hypotheses a very different vibrational distribution results, which can be found, on the assumption that the ratio between the predissociation and photoemission lifetimes is independent of v. Indeed with the first hypothesis the vibrational distribution is given by the fitting procedure [see Fig. 3(a)]; with the second hypothesis, the population of the $v=1$ level is zero. Since the form of the continuous part in the released kinetic energy spectrum strongly depends on the vibrational distribution of the photon-emitting states, a test for both hypotheses is possible.[15] The continuous part of the spectrum has been calculated in a standard way.[16] The comparison with the experiment [see Fig. 3(b)] provides support to the first hypothesis. Accordingly the vibrational distribution of the $^3\mathrm{HeD}^*$ molecules is 1, 0.65, 0.18, 0.12, 0.08 for $v=0$, 1, 2, 3, and 4. Moreover, we conclude that predissociation of the $B^2\Pi^+$ state is insignificant. Since this state is likely to be produced in amounts similar to the populations of the $B^2\Pi^-$ and $A^2\Sigma^+$ states, it is concluded that the $B^2\Pi$ state (both components) preferentially decays via photoemission, while the A state decays via predissociation.

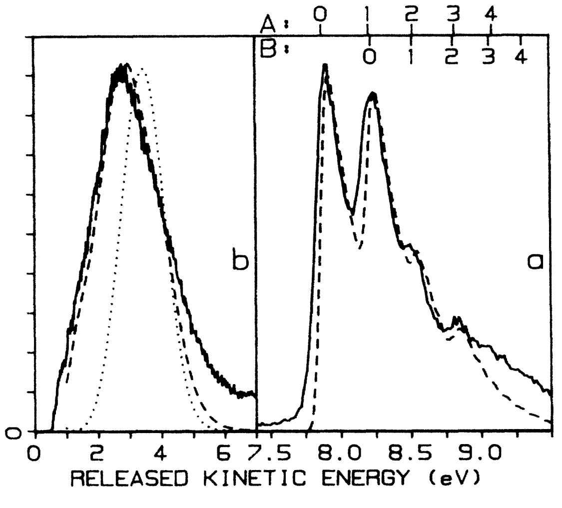

FIG. 3. Comparison between experimental released kinetic energy spectrum (full line) and simulations (dashed line). (a) High-energy region; the simulation involves for the total populations of the levels $A(v=0)$, $A(v=1)+B(v=0)$, $A(v=2)+B(v=1)$, . . . the values 1; 0.65; 0.18; 0.12; 0.08. The energies of the lowest vibrational levels of the A and B states are indicated in the upper part of the figure. (b) Low-energy region; the calculated spectra correspond to the hypotheses (i) (dashed line) and (ii) (dotted line) developed in the text. These calculations involve numerical determination of the overlap between bound and continuum nuclear wave functions weighted by both the vibrational distribution and the ν^3 factor (ν is the frequency of the emitted light).

We clearly observed strong radiative decay of the B state, and concluded that its predissociation is insignificant. However, we made calculations of the predissociative lifetimes by rotational coupling, indicating that predissociation should be competitive with radiative decay.[4] These calculations assume that the ground state retains its $2p\sigma$ character at small internuclear distances. The experimental observations may reflect the change of the ground-state character due to the avoided crossing with the A state.

Although a strong predissociation of the A state in ArH has been reported,[17] the interpretation has been placed in doubt by calculations by Theodorakopoulos *et al.*[3] Our results, however, clearly show that the A state predissociates. A calculation on the strength of the radial coupling that causes this predissociation would be of interest.

The authors want to thank Dr. J. R. Peterson and Dr. V. Sidis for several helpful discussions and critical reading of the manuscript. This work is sponsored by the Foundation for Fundamental Research on Matter, The Netherlands, with financial support by Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek. Laboratoire des Collisons Atomiques et Moléculaires is Laboratoire associé No. 281 au Centre National de la Recherche Scientifique.

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