Predissociation of the $c\,{}^3\Pi_u$ State of H_2†

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A flight-time–difference method was used to measure the energy distribution of H-H fragment pairs arising from dissociative charge-exchange collisions of H_2^+ ions. The spectrum exhibits sharp peaks which coincide with the energies of vibrational levels of the $c\,{}^3\Pi_u$ state of H_2 above the dissociation limit of the ground state. Predissociation into the $b\,{}^3\Sigma_u$ state is the main decay channel of the $c\,{}^3\Pi_u$ state. The lifetime is estimated to be $\leq 10^{-8}$ sec.

Some years ago, Lichten[1,2] showed that the $c\,{}^3\Pi_u$ state of H_2 is metastable. The $v=0$ vibrational level of this state lies lower than any even-parity level of the triplet spectrum and radiative dipole transitions from this vibrational level are forbidden.[2] The lifetime of this level was measured by Johnson[3] to be about 1 msec. Transitions from higher vibrational levels can occur. Freis and Hiskes[4] found the radiative lifetimes of these levels to be of the order of 0.1 msec. They pointed out, however, that according to Kronig's selection rules the even rotational levels of orthohydrogen and the odd rotational levels of parahydrogen can decay by allowed predissociations into the $b\,{}^3\Sigma_u^+$ state. Lichten[5] concluded that these levels have lifetimes of $\sim 10^{-9}$ sec. Thus, they are not metastable. No experimental evidence for these predissociations has yet been given.

While time-of-flight techniques[6] can be used to measure the energy distributions of metastable dissociation fragments the method fails when both fragments are formed in the ground state. For the investigation of the collision-induced dissociation of molecular ions we use a flight-time–difference method[7] to measure the angle and energy distributions of both charged and neutral dissociation fragments. The neutral fragments may be in their ground state as well.

In this experiment H_2^+ ions are extracted from a uniplasmatron ion source, accelerated to 5 keV and fired through a static H_2 gas target. The flight-time differences between the two dissociation fragments arriving at two separate detectors are measured. The detector consists of a CuBe sheet whose emitted secondary electrons are multiplied by a channeltron. By applying a rejecting field in front of the detector one can discriminate between charged and neutral particles.

Figure 1 shows the energy distribution of the H-H fragment pairs formed by dissociative charge-exchange collisions. The plot has been derived from the measured flight-time–difference spectrum. It gives the number of H atoms flying into the solid-angle element $d\omega$ with respect to the center of mass of the H_2^+ ion when an energy between ϵ and $\epsilon + d\epsilon$ is released as kinetic energy of both fragments in the center-of-mass frame. Since the scattering angle in the laboratory frame was not zero but 0.3°, the scattering angle θ in the center-of-mass frame changes along with ϵ. The most interesting feature is the small maximum at about 8 eV. This maximum is shown with higher resolution in Fig. 2, which reveals three resolved peaks which coincide very well with the energy of the lower vibrational levels of the $c\,{}^3\Pi_u$ state[8] above the dissociation limit of the ground state. The peaks are
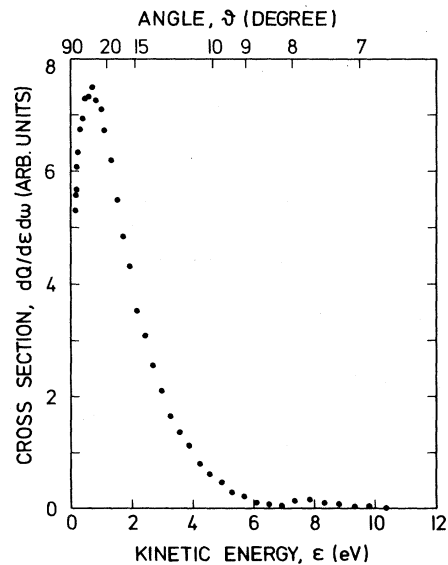

FIG. 1. c.m.-frame energy distribution of H-H fragment pairs arising from collisional dissociation of 5-keV H_2^+ ions incident on H_2 for a laboratory-frame scattering angle of 0.3°. The c.m.-frame scattering angle δ changes along with the kinetic energy of the fragments, ϵ.
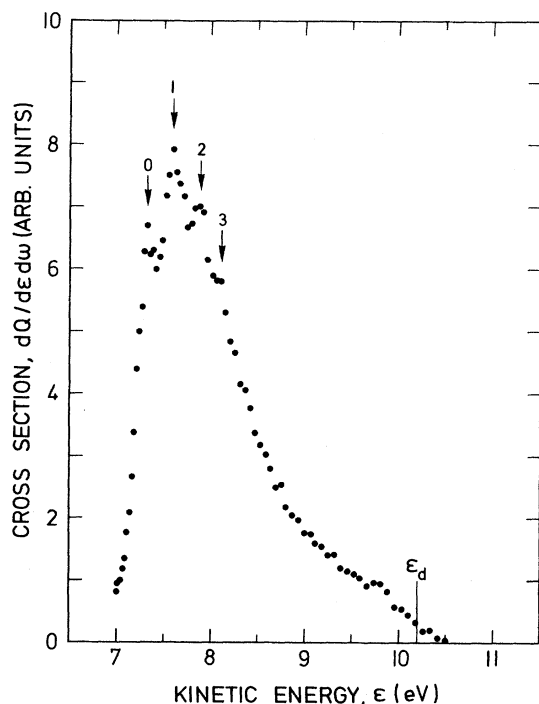
FIG. 2. A section of Fig. 1 with higher resolution. The arrows indicate the energies of the lower vibrational levels of the $c\,^3\Pi_u$ state above the dissociation limit of the ground state. ϵ_d is the dissociation limit of the $c\,^3\Pi_u$ state.

shifted by 0.04 eV to higher energies with respect to the ground rotational level, possibly due to the plasma temperature in the ion source. The accuracy of the energy scale, however, is of the same magnitude. The resolution is not sufficient to resolve higher vibrational levels, but they are no doubt present. The number of counts was about 3000 in the maximum of Fig. 2.

The plot goes across the dissociation limit of the $c\,^3\Pi_u$ state at 10.2 eV and approaches the abscissa at 10.5 eV. The superposition of the following processes might cause this effect: (1) Predissociations of higher electronic states, (2) the excitation of high rotational levels in the collision, thus forming a potential barrier, (3) the existence of high rotational levels in the H_2^+ beam, and (4) dissociations of H_2 molecules formed in doubly excited states. More measure-

ments on this effect will be presented in a forthcoming paper.

Finally, we estimated the lifetime of the predissociating levels. Using a shield between the collision chamber which has a length of 1.5 cm and one detector, this detector viewed an adjustable length of the neutralized H_2 beam inside as well as behind the collision chamber. The smallest beam length viewed by this detector was 0.5 cm, beginning at the entrance aperture of the collision chamber. No variation of the intensity ratio of the predissociation maximum in Fig. 1 to the low-energy maximum at 0.7 eV was observed. Since the particle velocity is about 0.7×10^8 cm/sec we conclude that the lifetime of the predissociation maximum is at the most 10^{-8} sec larger than the lifetime of the low-energy maximum. We suppose that the main fraction of the low-energy maximum are "fast" dissociations which take place after the collision within the time of a vibrational period of the nuclei. This will be the case when the H_2 molecule is formed in the repulsive $b\,^3\Sigma_u^+$ state or in the vibrational continuum of the electronic ground state. Thus, 10^{-8} sec is an upper limit of the lifetimes of the predissociating levels of the $c\,^3\Pi_u$ state. Since the radiative lifetimes of the vibrational levels above $v = 0$ were calculated[4] to be of the order of 0.1 msec we conclude that predissociation is the main decay channel of all vibrational levels of those H_2 molecules in the $c\,^3\Pi_u$ state which can decay by allowed predissociations.

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