First Spectroscopic Observation of the $C^2\Pi_u$ Excited State of H_2^+

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The translational-energy spectroscopy is used to search for the first transitions from the $X^2\Sigma_g$ ground state of H_2^+ to bound excited electronic states. Electron impact is used to create the H_2^+ ions from CH_4. It is known that electron impact on CH_4 creates H_2^+ ions highly rotationally excited. A transition is observed centered at 10.2 eV. The observed peak is assigned to the optically allowed transitions $X^2\Sigma_g^+ \rightarrow C^2\Pi_u$.

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The H_2^+ ion is the simplest molecule and as such its properties are of considerable fundamental importance. As a result, it has been the object of a large number of theoretical studies, of which a few of the pertinent ones are noted here.[1-3] One of the important predictions of these studies, first made by Teller,[3] is the existence of two stable bound states, $B^2\Sigma_g^+$ and $C^2\Pi_u$. Accurate theoretical spectroscopic constants for these states have been obtained.[2]

In addition to the fundamental interest in this ion, there is substantial interest in its spectroscopic properties for astronomical reasons.[4-6] The H_2^+ ion is expected to be a major component in stellar atmospheres as well as the upper atmospheres of hydrogen-rich planets such as Jupiter. Hence, its electronic spectrum is potentially of great astronomic importance.

Despite the fundamental and astronomic importance of the ion, there are no confirmed transitions reported between the $X^2\Sigma_g^+$ ground state and the $B^2\Sigma_g^+$ state (optically forbidden) or the $C^2\Pi_u$ state (optically allowed). There is one report of a possible H_2^+ transition in the far-ultraviolet spectrum of the star ζ-Tau[5] but this observation is almost certainly due to water impurity.[5,7] There have been calculations of the probable spectrum of H_2^+, both as Lyman-α sidebands in stars[4,7] and in Jupiter's atmosphere.[6] (A prediction of transitions between the $B^2\Sigma_g^+$ and $C^2\Pi_u$ excited states has been made by Kroll.[3])

The principle reason the electronic spectrum of H_2^+ has not been observed in the laboratory is that the equilibrium separations of the two excited states are very much greater than for the ground states[1-3]: $r_e(B^2\Sigma_g^+) = 4.7$ Å; $r_e(C^2\Pi_u) = 4.2$ Å; $r_e(X^2\Sigma_g^+) = 1.06$ Å. Hence the Franck-Condon factors are very small for all transitions except those originating from very excited $X^2\Sigma_g^+$. Theory[4,6,7] suggests that vibrational states of $H_2^+(X^2\Sigma_g^+)$ of $v = 18$ may be required for low values of J.

We decided to approach the problem using translational-energy spectroscopy[8,9] (TES). Our instrument has been described in detail previously.[10] Briefly, ions are formed by electron impact in an ion source, extracted, accelerated to 8 kV, mass selected by a magnet, injected into a collision cell filled with a variable pressure of He gas and located at the intermediate focus, passed through a high-resolution electrostatic energy analyzer (ESA), and detected by single-ion counting techniques. TES spectra are obtained by scanning the ESA at energies near the energy of the ion being investigated. Inelastic electronic transitions appear as peaks to lower translational energy. Peaks can occur due to excitation of either the ion beam or the neutral collision gas. Ultimate resolution on our instrument is ~0.1 eV. In this work 0.6 eV was utilized for signal-to-noise reasons.

We first chose to form H_2^+ from H_2 since it is known[11] that H_2 forms substantial amounts of vibrationally excited H_2^+ on electron impact. The TES spectrum obtained by use of He collision gas is given in Fig. 1. The only transitions observed

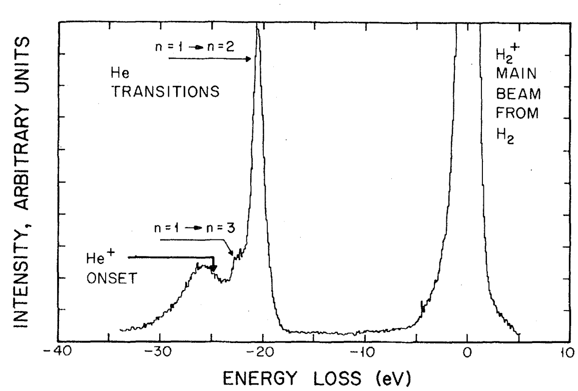

FIG. 1. Translational-energy-loss spectrum for H_2^+ formed from H_2. The H_2^+ main beam has an intensity of $\sim 7\times10^5$ counts and the most intense He transition, $\sim 2\times10^3$ counts. The resolution is ~ 0.3 eV.

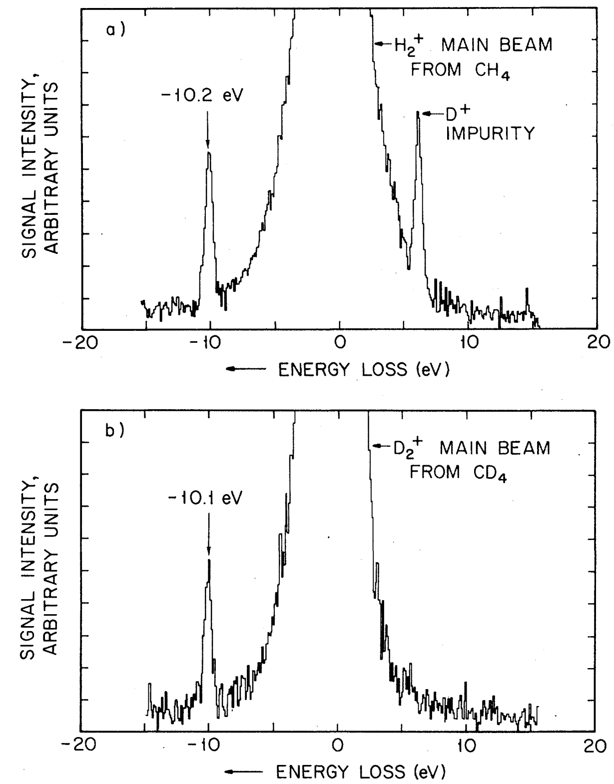

FIG. 2. (a) Translational-energy-loss spectrum for H_2^+ formed from CH_4. The feature at an apparent energy gain of 6 eV is due to a trace D^+ impurity (because of its slightly larger mass, D^+ is focused at a slightly higher energy than H_2^+; the D^+ ion has no TES spectrum and serves as a useful check on energy calibration). The main beam has an intensity of $\sim 7\times 10^5$ counts, and the feature at an energy loss of 10.2 eV has $\sim 7\times 10^2$ counts. The resolution is 0.6 eV. (b) Identical to (a) except for D_2^+ from CD_4. Note the absence of the D^+ peak.

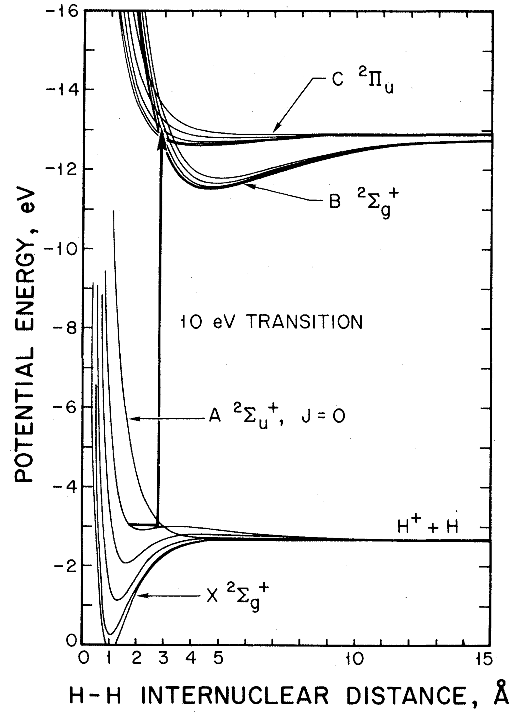

FIG. 3. A plot of potential energy vs H-H internuclear distance for the four lowest energy electronic states of H_2^+. For the $X^2\Sigma_g^+$, $B^2\Sigma_g^+$, and $C^2\Pi_u$ states curves are shown for $J=0$, 10, 20, 30, and 40. In each case rigid-rotor rotational constants were used. The transition drawn is purely for demonstration purposes and is not meant to imply a spectroscopic assignment.

occur between energy losses of 19 and 30 eV and can be unambiguously assigned to excitation of the He collision gas.

Beynon and co-workers,[12] however, have recently reported that highly rotationally and vibrationally excited H_2^+ can be formed by electron-impact dissociative ionization of CH_4: $CH_4 + e^- \rightarrow H_2^+ + CH_2 + 2e^-$. The H_2^+ ions so formed have substantial population in $J>30$. Hence we formed a beam of H_2^+ from electron impact on CH_4 and obtained the TES spectrum given in Fig. 2(a). This spectrum is identical with that given in Fig. 1 except for the feature centered at an energy loss of 10.2 eV with a full width at half height of 0.65 eV. (The He transitions, not shown, are identical with those in Fig. 1.) There are no possible transitions in He at 10.2 eV and there can be no impurities in the ion beam at mass 2 (except D^+ which has no TES spectrum; the trace D^+ impurity is, in fact, useful for calibrating the energy scale). Hence this feature must be due to a transition(s) in H_2^+.

It would be instructive to be able to construct H_2^+ potential curves for high J values. Unfortunately the best available theoretical corrections[1,2,7] for centrifugal distortion are useful only for $J \lesssim 10$. We are in the process of generating a new set of potential curves at high J. For the present a schematic presentation of H_2^+ potential energy curves for high values of J can be obtained with use of the rigid-rotor rotational constants. A set of such curves is given in Fig. 3 with a 10.2-eV transition drawn in. From such curves it appears that high-v, high-J, or high-v/medium-J conditions can all lead to significant Franck-Condon factors for the $X^2\Sigma_g^+ \rightarrow C^2\Pi_u$ transition.

Preliminary experiments have also been performed on D_2^+ from CD_4 and HD^+ from CD_3H. In both cases transitions are observed at about 10.2 eV in complete agreement with the H_2^+ results. An example of the D_2^+ spectra is given in Fig. 2(b). A transition is not observed at 10.2 eV for D_2^+ from D_2.

The transition that we observe has a width of ~0.65 eV, essentially equal to the resolution of this experiment (0.6 eV). Hence, it is not yet possible to determine the natural width of the transition. Modifications are underway in our detection system that should allow examination of the 10.2-eV transition at our ultimate resolution of 0.1 eV.

It appears that we are observing a relatively dense cluster of transitions from v,J states in $X^2\Sigma_g^+$ to v',J' in $C^2\Pi_u$. High-resolution spectroscopic studies in this energy region will be required to obtain detailed assignments and spectroscopic constants for high-J transitions. These will be very challenging experiments because it is difficult to obtain intense H_2^+ beams with high-v, high-J concentrations and spectroscopic light sources at 10 eV are not easily available. These high-resolution studies will also be required if H_2^+ lines in stellar spectra are to be identified and assigned.[13]

In summary, the first experimental observation has been made of bound-bound transitions between the $X^2\Sigma_g^+$ state and the $C^2\Pi_u$ state of H_2^+. Such transitions are not Franck-Condon accessible from the v,J states of H_2^+ obtained by electron impact on H_2. Large populations of high-J and possibly high-v states are required. Electron impact on CH_4 creates H_2^+ in such states and allows observation of the transition with use of TES. Further work is in progress and a complete report will be published in the future.

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[1] C. L. Beckel, B. D. Hansen, and J. M. Peek, J. Chem. Phys. 53, 3681 (1970).

[2] C. L. Beckel, M. Shafi, and J. M. Peek, J. Chem. Phys. 59, 5288 (1973); M. Shafi and C. L. Beckel, J. Chem. Phys. 59, 5294 (1973).

[3] D. M. Bishop and R. W. Wetmore, Mol. Phys. 26, 145 (1973); E. Teller, Z. Phys. 61, 458 (1930); M. Kroll, J. Mol. Spectrosc. 35, 436 (1970).

[4] J. C. Stewart, J. M. Peek, and J. Cooper, Astrophys. J. 179, 983 (1973).

[5] S. R. Heap and T. P. Stecher, Astrophys. J. 187, L27 (1974).

[6] F.-M. Wu, C. L. Beckel, M. Sharp, and C. L. Hyder, Icarus 22, 220 (1974).

[7] D. M. Bishop, S.-K. Shih, C. L. Beckel, F.-M. Wu, and J. M. Peek, J. Chem. Phys. 63, 4836 (1975).

[8] For a review of early work see J. P. Doering, Ber. Bunsenges. Phys. Chem. 77, 593 (1973).

[9] See, for example, J. H. Moore, Jr., and J. P. Doering, J. Chem. Phys. 52, 1692 (1970); J. H. Moore, Jr., J. Phys. Chem. 76, 1130 (1972), and Phys. Rev. A 8, 2359 (1973), and 10, 724 (1974).

[10] A. J. Illies and M. T. Bowers, Chem. Phys. 65, 281 (1982).

[11] F. Busch and G. H. Dunn, Phys. Rev. A 5, 1726 (1972).

[12] A. G. Brenton, J. H. Beynon, E. G. Richard, and P. G. Fournier, J. Chem. Phys. 79, 1834 (1983); J. H. Beynon, A. G. Brenton, and F. M. Harris, Int. J. Mass Spectrom. Ion Phys. 45, 5 (1982).

[13] See, for example, W. H. Brune, G. H. Mount, and P. D. Feldman, Astrophys. J. 227, 884 (1979).