Measured Densities and Rotational Temperatures of Metastable H_2 in a Multicusp Ion Source

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We report the first successful application of resonant multiphoton ionization to the diagnosis of a discharge. This technique is used to measure rotational temperatures of H_2 in the metastable $c\ ^3\Pi_u^-$ state, which are in the range of 400 to 600 K. The density of these molecules is determined by a single-photon ionization process, yielding a value of 3×10^9 cm^{-3} at a discharge current of 30 A. The relevance of these metastable molecules to H^- production in hydrogen discharges is discussed.

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The different approaches[1] to the production of technologically significant intense beams of fast neutral hydrogen atoms have converged to the generation of H^- ions in the so-called "volume" sources, containing magnetically confined H_2 plasmas. The H^- ions are extracted, accelerated to the required energy, and subsequently efficiently neutralized.[1] Such neutral beams are particularly relevant for heating and diagnostic applications in fusion plasmas.[1] In order to explain the abundance of H^- ions in hydrogen discharges,[2] it is commonly accepted, but experimentally not proven, that these ions are produced through dissociative electron attachment (DA) to vibrationally excited electronic ground-state hydrogen molecules[3] $[X\ ^1\Sigma_g^+(v'')]$. The cross section for this reaction increases strongly with the vibrational quantum number up to $v''=6$.[4] To test this hypothesis, the vibrational distribution of hydrogen molecules in such a discharge has to be measured and compared with calculated distributions.[3] Pealat *et al.*[5] measured this distribution up to $v''=3$ using coherent anti-Stokes Raman spectroscopy. We have set up an experiment to measure this distribution using resonant multiphoton ionization (RMI), which is a new technique in this field. The possibility of detecting molecular hydrogen in a quantum-state-specific manner with RMI was first demonstrated by Marinero, Rettner, and Zare.[6] Our experiment obtained the first successful measurement using this technique to diagnose conditions in a discharge. We were able to detect ground-state molecules, up to $v''=3$,[7] in a three-photon excitation, one-photon ionization scheme [(3+1) RMI]. In spite of that success, the measurements did not improve on the data given by Pealat *et al.*,[5] so we just mention them here. However, we have also successfully detected metastable $c\ ^3\Pi_u^-$ molecules in the same discharge, and we concentrate on that work in this Letter.

To distinguish between the different quantum states in $c\ ^3\Pi_u^-$, we used a one-photon excitation, one-photon ionization scheme, (1+1) RMI, and we were able to obtain the rotational temperature (T_r) of these molecules in $v''=0$, 1, and 2. In addition, we employed a nonresonant, one-photon ionization process to ionize $c\ ^3\Pi_u^-$ molecules irrespective of their quantum state. From this measurement we deduce the total $c\ ^3\Pi_u^-$ density. An interesting result of this work is the indication that metastable H_2 molecules may play a more significant role in the production of H^- ions in discharges than has been considered so far.[8,9] Moreover, our results provide additional experimental information that can be used as a test for theoretical models.[3]

A detailed description of the experiment will be given in a forthcoming paper.[10] A laser beam is focused approximately 5 mm in front of an aperture in the discharge chamber from which the gas-plasma mixture effuses. The detector is only sensitive to ions produced in a small volume around the laser focus. A magnetic field of ≈ 1 T at the laser focus prevents charged plasma particles from reaching this volume. An electric field of ≈ 1 MV/m accelerates along the magnetic field lines the atoms or molecules, ionized in the laser focus, into a lens system which transports them to the detector. The ion source is a magnetic multipole bucket source[1] with dimensions of $14\times14\times19$ cm^3. It can be operated up to 30 A, 200 V dc. The pressure in the source is varied between 0.1 and 5 Pa.

Specific quantum states of $c\ ^3\Pi_u^-$ were detected by (1+1) RMI measurements in the wavelength region from 570 to 605 nm. We found the one-photon excitations from $c\ ^3\Pi_u^-$ to all four $n=3$ triplet *gerade* states in hydrogen. In addition many of the peaks in the spectra we recorded correspond to the electric-dipole–forbidden transition $c\ ^3\Pi_u^- \rightarrow d\ ^3\Pi_u$, whose wavelengths were calculated from energy levels given in Ref. 11. In Fig. 1 we give the Q branches for the (0-0), (1-1), and (2-2) vibrational bands of this transition. Most of the P and R lines for these bands were also found in the spectra. We investigated the nature of the electric-dipole–forbidden transition $c\ ^3\Pi_u^- \rightarrow d\ ^3\Pi_u$ and found that it is of the enforced dipole type,[12] induced by the electric field of our detection system. Calculations[13] show that electric fields of the order of 1 MV/m are already strong enough to couple the $c\ ^3\Pi_u^-$ and the $a\ ^3\Sigma_g^+$ states. This coupling reduces the lifetime of $c\ ^3\Pi_u^-(v''=0)$ by a factor of ≈ 3 (to $\approx 300\ \mu$sec),[13] which apparently weakens the selec-

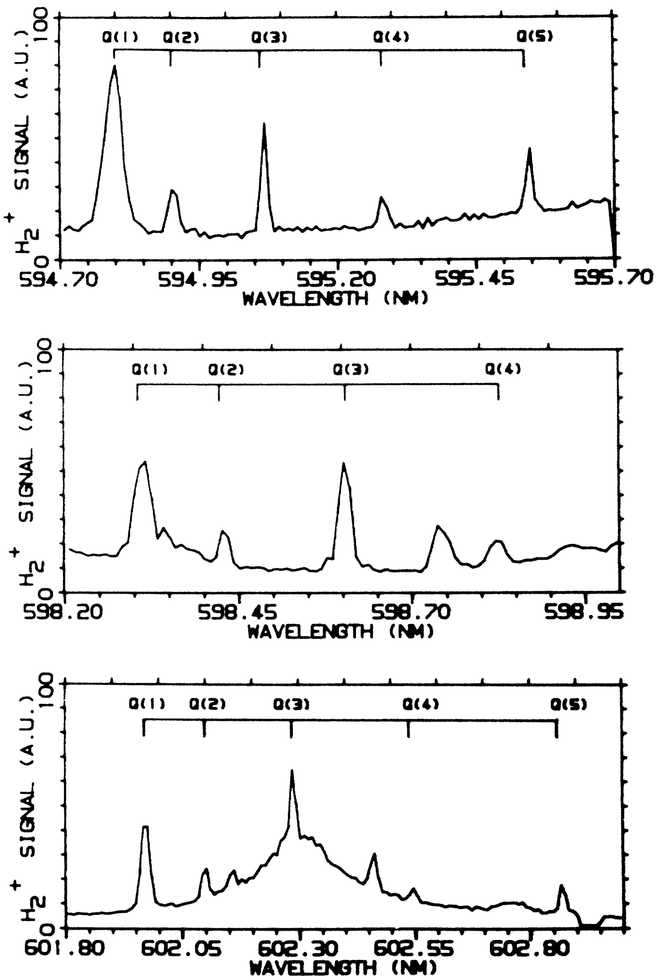

FIG. 1. $H_2{}^+$ signals obtained by employment of (1+1) RMI. Indicated are the line positions of the Q members of the (0-0), (1-1), and (2-2) vibrational bands (from above to below respectively) for the $c\,{}^3\Pi_u^- \rightarrow d\,{}^3\Pi_u$ transition. Discharge parameters for these measurements are arc current = 30 A, arc voltage = 100 V, and gas pressure = 0.4 Pa.

tion rule enough to allow the transition in our system. However, quenching of $c\,{}^3\Pi_u^-$ by this field can be neglected, as the molecules drift in $\approx 30\ \mu$sec from the middle of the discharge to the laser beam.

We decided to deduce T_r from the forbidden transitions as these peaks are well resolved in contrast to the peaks of the allowed transitions. In addition, the rotational branches for the forbidden transition appear in conveniently small wavelength regions. To determine T_r, we fitted the amplitudes $A(J'')$ of the peaks, from a measurement as in Fig. 1, by a Boltzmann distribution. The result for the $v''=2$ scan in Fig. 1 is presented in Fig. 2. The amplitudes are corrected for the degeneracy of the rotational levels $(2J''+1)$ and nuclear spin states $(2T+1)$. The rotational line strengths are not known to us for the forbidden transitions, and therefore we have taken them to be equal. It is seen that the data points

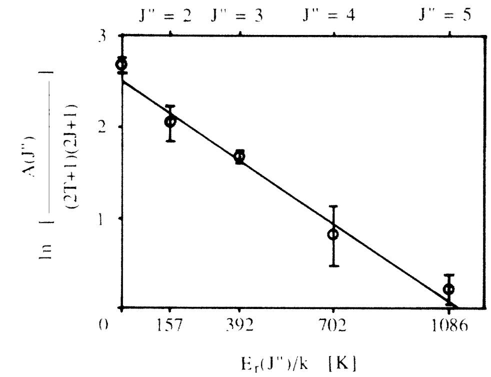

FIG. 2. Boltzmann plot for the $v''=2$ measurement in Fig. 1. The slope of the straight line corresponds to $T_r=450$ K.

fall on a straight line, which we consider as a justification for the procedure.[6] The slope of the straight line, which is fitted to the data by the least-squares criterion, gives $T_r=450$ K. From the uncertainty in the individual data points we can estimate the error in the temperatures to be $\approx 10\%$. The results for the variation of T_r for $c\,{}^3\Pi_u^-$ with arc current is given in Table I. For comparison, we also give T_r for $X\,{}^1\Sigma_g^+(v'')$ obtained with (3+1) RMI in the same discharge. The temperatures for $X\,{}^1\Sigma_g^+(v'')$ as obtained by Pealat *et al.*[5] are in the same range as ours. We note that Table I shows a peculiar difference in the variation of T_r with v'': At constant arc current and increasing v'', T_r increases for $X\,{}^1\Sigma_g^+(v'')$, whereas it decreases for $c\,{}^3\Pi_u^-(v'')$. Apparently, metastable hydrogen is rotationally colder than the ground state. Rotational cooling has been observed[14] in the excitation of $H_2{}^+$ from $X\,{}^1\Sigma_g^+$, and is associated with the reduction in the rotational constant. The behavior in our experiment is not yet completely understood. It may include an indication that $X\,{}^1\Sigma_g^+$ and $c\,{}^3\Pi_u^-$ are involved in different reaction mechanisms. Further measurements are needed to clarify this point.

To obtain the total $c\,{}^3\Pi_u^-$ density in the discharge we used photons at $\lambda=337$ nm. These photons have enough energy to ionize $c\,{}^3\Pi_u^-$ in a one-photon process, regard-

TABLE I. Rotational temperatures (in kelvins) for $X\,{}^1\Sigma_g^+(v''=0,1,2)$ and $c\,{}^3\Pi_u^-(v''=0,1,2)$ for different arc currents. Other discharge parameters are arc voltage, 100 V, and pressure, 0.4 Pa, in the case of metastable hydrogen $c\,{}^3\Pi_u^-$, and 1.2 Pa in the case of $X\,{}^1\Sigma_g^+$.

Arc current (A)	State	$v''=0$	$v''=1$	$v''=2$
10	$X\,{}^1\Sigma_g^+$	460	560	640
	$c\,{}^3\Pi_u^-$	460	440	360
20	$X\,{}^1\Sigma_g^+$	530	680	750
	$c\,{}^3\Pi_u^-$	500	500	380
30	$X\,{}^1\Sigma_g^+$	600	750	900
	$c\,{}^3\Pi_u^-$	570	570	450

less of their quantum state. At this wavelength the dye laser delivers a high enough pulse energy to saturate this ionization process. Careful determination[10] of such factors as the size of the acceptance volume of the detector, the current corresponding to one single ion, the overall efficiency of the detection system, and the rate of expansion of the gas effusing from the source allowed us to relate the detector signal to the $c\,^3\Pi_u^-$ density. A result is presented in Fig. 3. Because of uncertainties in the detection efficiencies, the $c\,^3\Pi_u^-$ density should be regarded as approximate, and in fact is a lower limit. The relative values, however, are accurate within $\approx 10\%$.

Hiskes, Bacal, and Hamilton[8] have made an estimate for the ratio of the $c\,^3\Pi_u^-$ density to the gas density in a discharge and found an upper limit of 2×10^{-5}, from which we calculate the predicted upper limit of the $c\,^3\Pi_u^-$ density in our discharge to be $\approx 10^9$ cm^{-3} at 0.4 Pa. Although this is consistent with our experimental density ($\approx 3\times10^9$ cm^{-3}) it should be recalled that we consider the latter as a lower limit.

The variation of the $c\,^3\Pi_u^-$ density with neutral gas pressure and arc current can qualitatively be understood when we consider an approximate expression for the equilibrium density n_c of $c\,^3\Pi_u^-$ molecules,

$$n_c \approx \frac{n_g n_p \langle \sigma_c v_p \rangle}{v_c/L + n_g n_p \langle \sigma_i v_p \rangle \tau^+ \langle \sigma_a v_e \rangle + n_g \langle \sigma_+ v_g \rangle}, \qquad (1)$$

where n_g and n_p are the densities for neutral gas and primary electrons and v_p, v_e, v_c, and v_g give the speed of primary electrons, plasma electrons, $c\,^3\Pi_u^-$, and $X\,^1\Sigma_g^+$ respectively. The reaction rates for excitation (to $c\,^3\Pi_u^-$) and ionization of $X\,^1\Sigma_g^+(v''=0)$ (by primary electrons) is given by $\langle \sigma_c v_p \rangle$ and $\langle \sigma_i v_p \rangle$. The reaction rate for collisional excitation of $c\,^3\Pi_u^-$ to the close-lying, short-living (≈ 10 nsec) $a\,^3\Sigma_g^+$ state by plasma electrons is $\langle \sigma_a v_e \rangle$. The cross section for this process is expected to be quite large ($\approx 10^{-13}$ cm^2), because of the small energy difference between these two states.[9] $\langle \sigma_+ v_g \rangle$ is the reaction rate for the process $c\,^3\Pi_u^- + X\,^1\Sigma_g^+ \rightarrow c\,^3\Pi_u^+ + X\,^1\Sigma_g^+$ after which $c\,^3\Pi_u^+$ predissociates. L is the mean distance to the wall and τ^+ is the positive-ion lifetime. In (1) the plasma electron density n_e is approximated by the positive-ion density $n_+ \approx n_g n_p \langle \sigma_i v_p \rangle \tau^+$. The numerator of (1) gives the mechanism for the production of $c\,^3\Pi_u^-$ by primary electrons. The three terms in the denominator present the losses suffered by collisions with the walls, plasma electrons, and neutral gas molecules, respectively. In addition, one should realize that $\langle \sigma_c v_p \rangle$ and $\langle \sigma_i v_p \rangle$ are affected by n_g because of energy degradation of the primary electrons with increased density. Following a similar calculation as was done by Bacal, Bruneteau, and Nachman,[2] it can be shown that this effect becomes important if $p > 0.2$ Pa. Above this pressure $\langle \sigma_c v_p \rangle$ and $\langle \sigma_i v_p \rangle$ will decrease with increasing pressure.

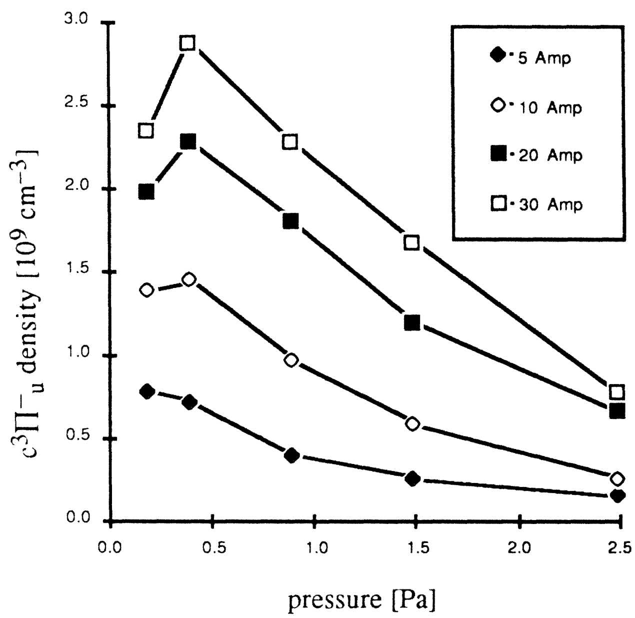

FIG. 3. Variation of $c\,^3\Pi_u^-$ density with neutral gas pressure for different arc currents. Discharge voltage is 100 V.

At low pressure, the loss rate by wall collisions will dominate over the other two loss mechanisms and consequently (1) predicts that n_c will be proportional to n_g and n_p which is also seen in Fig. 3 for $p < 0.4$ Pa. At higher pressures wall losses of $c\,^3\Pi_u^-$ are negligible and the explicit dependence of (1) on n_g drops out. However, because of energy degradation of the primary electrons ($\langle \sigma_c v_p \rangle$ and $\langle \sigma_i v_p \rangle$ decrease), n_c decreases with increasing pressure, as is also the case in Fig. 3 for $p > 0.4$ Pa. In addition (1) predicts that n_c will flatten out with increasing n_p. This effect is clearly seen in our measurements if we plot the data given in Fig. 3 as a function of discharge current, at constant pressure.

Bacal, Bruneteau, and Nachman have investigated the variation of H^- density normalized to electron density versus H_2 pressure for several configurations of the magnetic multipole. It is interesting to note that for all three configurations studied this quantity exhibits a maximum at $p = 0.3$ Pa (Fig. 14 in Ref. 2), which is roughly the same value we find for the maximum of the $c\,^3\Pi_u^-$ density. Holmes, Dammertz, and Green found an optimum for the extracted H^- current at 0.5 Pa, which value falls in the same range again. These coincidences suggest that $c\,^3\Pi_u^-$ is related to H^- formation. In Ref. 8 it was calculated that DA to $c\,^3\Pi_u^-$ does not contribute significantly to the observed H^- density. However, Hiskes and Karo[9] have already pointed out that $c\,^3\Pi_u^-$ can be Auger deexcited at the wall, giving rise to the formation of vibrationally excited ground-state molecules which are effectively converted to H^- by DA.[4] They[9] calculated the rate with which triplet excitations populate $X\,^1\Sigma_g^+(v''=6-14)$ levels and compared this to the rate with which singlet excitations populate these levels. The triplet rate was found to be only a factor of 2 lower than the singlet rate, which indeed indicates the importance of $c\,^3\Pi_u^-$ in the volume production of H^- ions. In addition, collisional excitation of $c\,^3\Pi_u^-$ to singlet states ($C\,^1\Pi_u$ or $B\,^1\Sigma_u^+$) by plasma electrons, after which these states radiate back to the ground state, is a mechanism for population of the $X\,^1\Sigma_g^+(v''=6-14)$ levels. However, until now only singlet excitations have been held responsible for the production of highly vibrationally excited molecules.[3]

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[1]Wulf B. Kunkel, IEEE Trans. Nucl. Sci. **26**, 4166 (1979); K. W. Ehlers, J. Vac. Sci. Technol. A **1**, 974 (1983); A. J. T. Holmes, G. Dammertz, and T. S. Green, Rev. Sci. Instrum. **56**, 1697 (1985).

[2]M. Bacal, A. M. Bruneteau, and M. Nachman, J. Appl. Phys. **55**, 15 (1984).

[3]J. R. Hiskes, A. M. Karo, and P. A. Willmann, J. Appl. Phys. **58**, 1759 (1985); C. Gorse, M. Capitelli, J. Bretagne, and M. Bacal, Chem. Phys. **93**, 1 (1985).

[4]M. Allan and S. F. Wong, Phys. Rev. Lett. **41**, 1791 (1978); J. M. Wadehra and J. N. Bardsley, Phys. Rev. Lett. **41**, 1795 (1978), and Phys. Rev. A **20**, 1398 (1979).

[5]M. Pealat, J.-P. E. Taran, M. Bacal, and F. Hillion, J. Chem. Phys. **82**, 4943 (1985).

[6]E. E. Marinero, C. T. Rettner, and R. N. Zare, Phys. Rev. Lett. **48**, 1323 (1982).

[7]P. J. Eenshuistra, J. H. M. Bonnie, and H. J. Hopman, to be published.

[8]J. R. Hiskes, M. Bacal, and G. W. Hamilton, Lawrence Livermore Laboratory Report No. UCID-18031, 1979 (unpublished).

[9]J. R. Hiskes and A. M. Karo, University of California Radiation Laboratory Report No. UCRL-87779, 1982 (unpublished).

[10]J. H. M. Bonnie, E. H. A. Granneman, and H. J. Hopman, to be published.

[11]*The Hydrogen Molecule Wavelength Tables of G. H. Dieke,* edited by H. M. Crosswhite (Wiley, New York, 1972).

[12]R. H. Garstang, in *Atomic and Molecular Processes,* edited by D. R. Bates (Academic, New York, 1962).

[13]Robert P. Freis and John R. Hiskes, Phys. Rev. A **2**, 573 (1970).

[14]D. P. DeBruijn and W. Koot, private communication.