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LETTER TO THE EDITOR

The total excitation cross section of the c $^3\Pi_u$ state of H_2

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Abstract. The total excitation cross section for the c $^3\Pi_u$ ($v=0$) state is measured from threshold to 60 eV using a time of flight recoil technique.

Molecular excitation plays an important role in systems as diverse as the interstellar medium, planetary atmospheres and laser plasmas (Brown 1979), but in spite of this range of application there has been limited progress, both theoretically and experimentally, in the study of electron–molecule collisions (Trajmar *et al* 1983, Massey 1983). Recently, however, computational techniques have developed to such an extent that there is now a need for accurate experimental data with which to make comparisons. Current theoretical effort has concentrated on the relatively simple H_2 molecule: the excitation cross sections of some of its states have been calculated by a variety of methods. The b $^3\Sigma_u^+$ state excitation cross section has been determined by Baluja *et al* (1985) using the *R*-matrix method, by Schneider and Collins (1985) using a linear algebraic method and by Lima *et al* (1985) by application of the Schwinger multichannel variational method. However, the b state—as with the other states of H_2 recently considered theoretically (e.g. the a $^3\Sigma_g^+$, d $^3\Pi_u$, e $^3\Sigma_u^+$ and B $^1\Sigma_u^+$ (Chung *et al* 1975, 1978))—requires complex detection techniques to select the photons emitted when these states decay in any experimental measurement of the cross section. The c $^3\Pi_u$ state of H_2 is metastable and hence the excitation cross section may be determined by direct detection of the metastables produced using a conventional channel electron multiplier.

The existence of a metastable state in molecular hydrogen was first determined by Lichten (1957, 1960), using the molecular beam magnetic resonance technique. An examination of the term scheme for H_2 with the selection rules for diatomic molecules shows that no known state except c $^3\Pi_u$ is metastable. The lowest excited state, b $^3\Sigma_u^+$, is repulsive and dissociates in approximately 10^{-14} s into two ground-state hydrogen atoms, while the B $^1\Sigma_u^+$ state decays via an allowed transition with a lifetime of the order of 10^{-10} s to the ground state X $^1\Sigma_g^+$. The a $^3\Sigma_g^+$ state decays by an allowed transition to the repulsive triplet state in approximately 10^{-8} s. All other states of H_2 decay via allowed transitions to the ground state of H_2 or to repulsive states. Dissociative excitation can produce hydrogen atoms in the metastable 2S state; however, these atoms are quenched selectively by small electric or magnetic fields and are not detected in the present experiment. The lowest vibrational level ($v=0$) of the c $^3\Pi_u$ state can only decay to the b $^3\Sigma_u^+$ state via a forbidden magnetic dipole transition and the lifetime for such a transition is of the order of milliseconds. Consequently, at room temperature with the thermal velocity of H_2 approximately equal to 2×10^5 cm s^{-1}, the decay length

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should be of the order of metres, making the $c\,^3\Pi_u$ ($v = 0$) state easily detectable beyond its point of formation. Higher vibrational levels ($v \geqslant 1$) of $c\,^3\Pi_u$ can decay to $a\,^3\Sigma_g^+$ and so are unlikely to be long lived, although the rate of the transition ($a\,^3\Sigma_g^+ \leftarrow c\,^3\Pi_u$) could give the $c\,^3\Pi_u$ ($v = 1$) a semi-metastable lifetime. Recent work in this laboratory (Mason and Newell 1986a) on negative-ion resonance formation in the total excitation cross section of the $c\,^3\Pi_u$ state provided no evidence to suggest that this state is metastable with a lifetime $\tau \geqslant 1\ \mu s$, and if it is relatively long lived with $\tau < 1\ \mu s$ it will not be detected in the present apparatus.

The experimental arrangement used consists of an electron gun (Mason and Newell 1986b) which produces a beam of 1 μA at 6 eV incident on an electrostatic hemispherical monochromator. The monochromated electron beam is then accelerated to the required impact energy and intersected at right angles with a molecular hydrogen gas beam produced by a hypodermic needle. Spectroscopic grade gas was used in all experiments. Since there is a net momentum transfer to the metastable molecular beam it is necessary to place the detector at an angle which accommodates the effect of the momentum transfer to the metastable molecules, to ensure that all those produced are detected. The channel electron multiplier is therefore placed at a scattering angle $\theta = 73°$ with respect to the incident electron beam direction. A full account of the present time of flight recoil technique is given in a separate paper on metastable excitation cross sections in the rare gases (Mason and Newell 1986c).

A 10 V, 100 μs negative pulse applied to a gun lens is sufficient to modulate the electron beam. The time of flight spectra consist of photons which arrive as a prompt pulse, followed by scattered electrons which arrive at the detector within 30 ns of the trailing edge of the primary electron pulse, and finally the metastable molecules and ions which have flight times of approximately 20 μs. The positive ions are removed by the application of a small positive voltage at the entrance to the detector. The data are stored as a time of flight spectrum on a multichannel analyser, then integrated over a finite time range and normalised to unit electron current. The excitation cross section presented here extends from threshold to 60 eV and at each measured energy the data have been corrected for both electron beam and gas beam variations. The present data have been placed on an absolute scale by normalising the peak to the cross section maximum in the work of Lee Mu-Tao *et al* (1982).

Although it is possible to determine the number density of the molecular gas beam it has not been possible to make the present data absolute since the detection efficiency of the channel electron multiplier for metastable hydrogen molecules is unknown.

In figure 1, the $c\,^3\Pi_u$ excitation cross sections determined using the present recoil technique are compared with earlier work. The occurrence of resonance series close to threshold (Mason and Newell 1986a, Comer and Read 1971) allows the energy scale to be accurately determined, with all contact potentials eliminated. This method of energy calibration is very accurate since the threshold for metastable production is detected at 11.75 eV, in excellent agreement with the spectroscopic value of 11.76 eV (Elston *et al* 1974). The present cross section is measured from threshold to 60 eV (the limit of most of the available theoretical data), thus extending the range of earlier work and providing evidence for the importance of metastable production in energy regions previously considered free of such effects (Clampitt 1969).

Lichten (1960) found the excitation cross section to peak sharply at approximately 15.5 eV, in agreement with Clampitt and Newton (1969), while Cermak (1966) detected the peak at 17 eV, in good agreement with the present work which places the peak at 16 eV. There are clear differences in the shapes of the various cross sections, especially

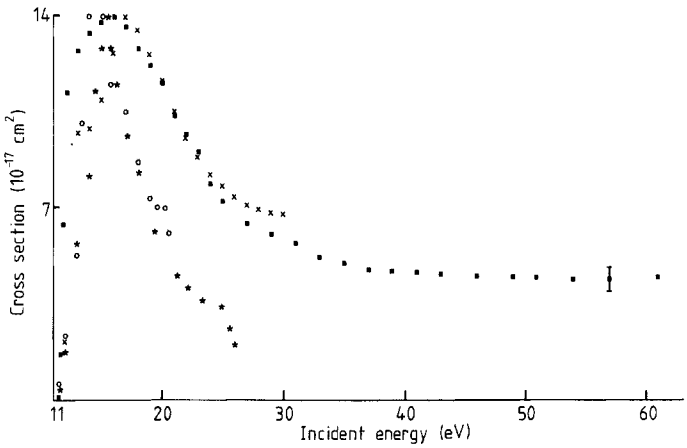

Figure 1. Total excitation cross sections for the c $^3\Pi_u$ state. Experiment: ■, present work; ×, Cermak (1966); ○, Clampitt and Newton (1969); *, Lichten (1960).

at higher energies, with the present data agreeing well with those of Cermak but disagreeing sharply with those of Lichten and of Clampitt and Newton. A possible explanation for the differences in the observed cross section shapes is the effect of recoil of the product metastable molecules combined with the gas beam direction and the observation angle of the detector. We are unfortunately not able to correct the experimental data of the other workers owing to inadequate information on the geometries of their experiments and the absence of information on the orientation of the momentum transfer vector, above threshold, as a function of the incident electron energy. The detection geometries of Lichten and of Clampitt and Newton are very selective in angle and would certainly highlight recoil effects in the measured total cross sections. Recoil effects are more dominant close to threshold (Borst 1974), and neither Lichten nor Clampitt and Newton stated that they had considered the experimental implications of this effect. The present cross section and Cermak's cross section have been carefully measured to exclude any recoil effects from the measured cross section; there is also excellent agreement between Cermak and the present group in the measurment of rare-gas metastable cross sections (Mason and Newell 1986c). Differential (0°, 180°) excitation functions of the c $^3\Pi_u$ state, corresponding to electron scattering angles of 0° and 180°, have recently been measured by Pasquerault *et al* (1985). A direct comparison with these data is not possible since these measurements relate to only two orientations of the momentum transfer vector, i.e. parallel and perpendicular to the incident electron beam direction, whereas the present data relate to all orientations of the momentum transfer.

The earliest theoretical treatment of the excitation cross section of the c $^3\Pi_u$ state is that of Khare (1967), who used the one-centre wavefunctions of Huzinaga (1957) with the Ochkur first-order exchange approximation to investigate the singlet-triplet excitations. His results predicted a peak at 14 eV, with a subsequent fall to zero at around 100 eV. Chung *et al* (1975) used the Born-Rudge approximation to calculate the c $^3\Pi_u$ excitation cross section; Chung and Lin (1978) later applied the close-coupling method, obtaining a cross section similar in shape to that of Chung but with a magnitude twice that of the Born-Rudge results. This work predicted a peak in the cross section at 14.5 eV.

Recently, Lee Mu-Tao *et al* (1982) used the distorted-wave approximation to calculate the $c\,^3\Pi_u$ excitation cross section. This calculation gives a peak at 20 eV, with a subsequent fall in the cross section to a plateau beyond 35 eV. These theoretical results are compared with the present experimental results in figure 2. At higher energies, cascade phenomena preclude any direct comparison, although the general trends may be observed.

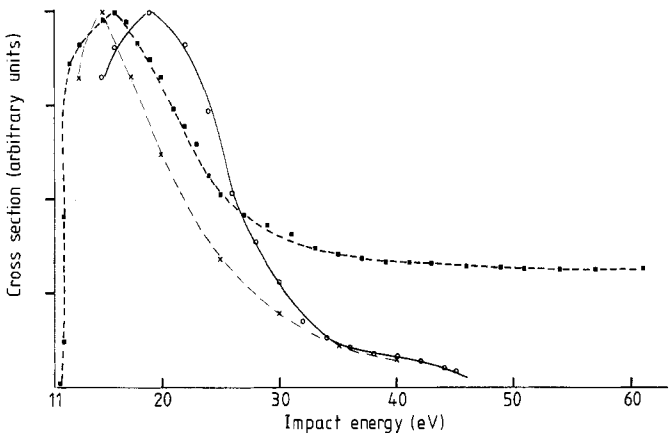

Figure 2. Total excitation cross sections for the $c\,^3\Pi_u$ state. Experiment: ■, present work. Theory: ×, Chung and Lin (1978); ○, Lee Mu-Tao *et al* (1982). See text for discussion.

Cascade into the $c\,^3\Pi_u$ ($v=0$) state at high electron energies can occur from any triplet state $^3\Lambda_g$ ($\Lambda=\Pi\pm1$) which exists above the $c\,^3\Pi_u$ state and for which the Franck–Condon principle is satisfied. The measured cross section above 30 eV clearly shows the effects of cascade when compared with the current theoretical calculations; quantification of the cascade contribution is not possible in the present work. Cascade contribution at the threshold will come mainly from the $a\,^3\Sigma_g^+$ state, which lies less than 1 eV above the $c\,^3\Pi_u$ level. However, since the excitation cross sections for the $c\,^3\Pi_u$ and the $a\,^3\Sigma_g^+$ are in a 6:1 ratio (Chung and Lin 1978) we would expect the cascade effect to be small. These calculations are supported by the energy loss work of Bose and Linder (1979) who have reported differential threshold measurements for these states. However, once the electron beam energy is approximately 2 eV above the $c\,^3\Pi_u$ threshold, states which can cascade into the $a\,^3\Sigma_g^+$ state are excited. Bose (1978) measured the optical decay of the $a\,^3\Sigma_g^+$ to the repulsive $b\,^3\Sigma_u^+$ and estimated that the contribution to the emitted light from the $e\,^3\Sigma_u^+$ state cascading into the $a\,^3\Sigma_g^+$ state was 20%. This effect is a factor of five smaller than the direct decay of the $a\,^3\Sigma_g^+$ state into the $c\,^3\Pi_u$ state; we would conclude therefore that the effect of cascade at the threshold of the cross section is small. The data of Chung *et al* (1975), Chung and Lin (1978) and Khare (1967) all agree closely and so only those of Chung *et al* are shown; all data in figure 2 are normalised to a peak intensity.

In this letter new experimental results for the excitation cross section of the $c\,^3\Pi_u$ metastable state of H_2 have been presented. While there appears to be a consensus between the present experimental work and that of Cermak regarding the shape of the cross section, there is definite disagreement with current theory, especially regarding the location of the cross section maximum.

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