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High-resolution studies of total electron excitation functions near threshold for the states $B\,^1\Sigma_u^+$ and $c\,^3\Pi_u$ of molecular hydrogen*

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Studies have been made of uv and metastable excitation functions for H_2 near threshold. Within 2 eV of threshold the total cross sections appear to be dominated by two vibrational series of resonances. In the excitation function of $B\,^1\Sigma_u^+$ (uv emitting), one series (band "a") is ten times more intense than the other (band "c"), while for $c\,^3\Pi_u$ excitation (metastable), the two series have approximately equal intensity. The measured energy positions of the resonant peaks agree well with results obtained by other experimental techniques and with theory. Energy calibration of the metastable excitation function has confirmed that the $c\,^3\Pi_u$ ($v=0$) level is metastable, and there was no obvious threshold for a second metastable vibrational level, although the nature of the data does not preclude its existence.

I. INTRODUCTION

Core-excited resonances play an important role in electron scattering by diatomic molecules. These resonances are regarded as a result of the temporary attachment of an incident electron to a parent excited electronic state of the target molecule, and the subsequent decay by autoionization, leaving the molecule in some energetically allowed final state. The diversity of decay channels permits the observation of these phenomena by a variety of experimental techniques. A comprehensive review has been given recently by Schulz.[1]

Molecular hydrogen is a particularly important target medium for these studies, since detailed theoretical models have been developed for many of the resonance phenomena.[2,3] In Fig. 1 we illustrate the potential energy curves for electronic states which are relevant to our work. The solid curves are for states of the neutral hydrogen molecule, while the dotted curves are for the pair of resonant states formed by temporary attachment of an incident electron to the parent states $c\,^3\Pi_u$ and $C\,^1\Pi_u$. The shapes of the curves for the compound states, as a function of internuclear separation, are expected to follow closely those of their respective parents, and hence they should have similar spacings between their vibrational components. These compound states manifest themselves as sharp resonances in scattering cross sections at electron-impact energies corresponding to their various vibrational levels. Several experimental studies have been made previously of the resonances associated with the compound states depicted in Fig. 1, and these have been summarized in the review by Schulz.[1] We shall give specific references in Sec. III, where detailed comparisons are made with our results. These particular vibrational "bands" of resonances have been labeled band a (parent $c\,^3\Pi_u$) and band c (parent $C\,^1\Pi_u$).

We have studied these resonances in the total excitation functions of the $B\,^1\Sigma_u^+$ and $c\,^3\Pi_u$ states. The data complements the information on differential excitation functions obtained by the electron energy-loss technique,[4] which has the advantage of being amenable to studies of angular distribution, thereby providing important information on the angular-momentum properties of the resonances. On the other hand, our work demonstrates resonant contributions to the total excitation, and gives the positions and intensities of the resonances averaged over all angles.

The vibrational components of band a appear as the principal features in $B\,^1\Sigma_u^+$ excitation near threshold, the relative intensities of band c being about a factor of 10 smaller. In a preliminary report[5] we gave the results of our observations with a windowless detector, showing the appearance of these resonances in the combined $B\,^1\Sigma_u^+$ and $c\,^3\Pi_u$ excitation functions. The $B\,^1\Sigma_u^+$ (uv-emitting) and $c\,^3\Pi_u$ (metastable) states were observed simultaneously by the detection method used at that time. The uv portion of our data showed qualitative similarity to earlier work by McGowan and Williams,[6] but these workers had incorrectly calibrated their energy scale, which resulted in an interchanged identification of bands a and c.

The work we report in this paper has improved energy resolution and several independent calibrations of the energy scale. In addition, the $B\,^1\Sigma_u^+$ and $c\,^3\Pi_u$ channels were separated (i) by placing an MgF_2 window over the detector to limit the data to uv photons emitted by the decaying $B\,^1\Sigma_u^+$ and (ii) by using a crossed-beam technique

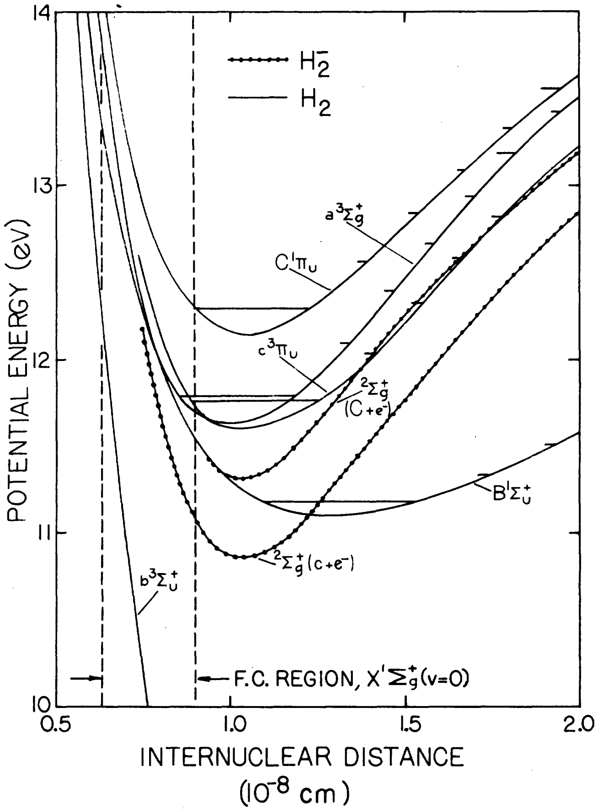

FIG. 1. Internuclear potential curves for H_2 which are relevant to the present work. The solid lines represent stable electronic states of the neutral molecule, and the broken lines are resonant states formed by the temporary attachment of the incident electron to designated parent states.

with a windowless detector, so that solid-angle considerations greatly enhanced the detection of $c\,^3\Pi_u$ metastables compared to photons from the $B\,^1\Sigma_u^+$ state. The metastable data showed for the first time that bands a and c appear with approximately equal intensities in the $c\,^3\Pi_u$ excitation function. A preliminary report of this work has appeared in abstract form.[7]

II. METHOD

A. Photon detection after excitation

Many aspects of our apparatus have been described in an earlier paper on excitation of metastable N_2.[8] Electrons from a hemispherical monochromator entered a gas target cell containing H_2 at a pressure of about 10^{-4} Torr. The incident-electron current was typically 10^{-9} A with an energy resolution full width at half-maximum (FWHM) of 0.04 eV. Photons resulting from the decay of excited states were detected by electron ejection from the cathode surface of a Channeltron electron multiplier, the entrance aperture of which was covered by an MgF_2 window 1.5 mm in thickness. The photon energy range over which this detection system had appreciable sensitivity was 8.5–11.3 eV, the lower limit being determined by the secondary emission properties of the Channeltron cathode, and the upper limit by the transmission of the MgF_2 window.

The detector signal, after pulse amplification and discrimination, could be registered on an XY recorder display, or stored digitally on punched tape. In the XY mode the signal was integrated by a count-rate meter with a time constant of 10 sec while the electron-impact energy was being swept at the rate of 5 eV/h. When the data was being stored on tape, the energy was stepped in 0.02-eV increments. Counts were accummulated for either 10 or 60 sec at each energy before being registered on the tape.

B. Metastable detection after excitation

A crossed-beam technique was used in conjunction with a windowless Channeltron detector as illustrated in Fig. 2. The axis of the Channeltron was set at an angle of 18° with respect to the direction of a collimated beam of H_2, such that metastable H_2 molecules would recoil towards the detector after excitation by the crossed beam of electrons.

The H_2 source was a Pyrex bulb containing the gas at a pressure of about 1 Torr. The beam was collimated by the alignment of apertures in a differential pumping chamber and in the scattering element of the monochromator with respect to a nozzle in the source. The total flow from the source was 10^{19} molecules/sec, and the beam density in the scattering region was estimated to be 10^9 molecules/cm^3.

Approximately 80% of the metastables excited recoiled into the detector. The solid angle subtended by the detector aperture at the scattering region was 0.12 sr, meaning that only 1% of the photons generated in the scattering region reached the detector. The geometric enhancement of metastable over photon detection was therefore a

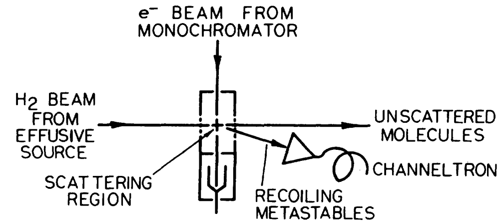

FIG. 2. Diagrammatic representation of the geometry of the e-H_2 crossed-beam experiment.

factor of 80. It is believed that the detection efficiencies of the Channeltron for photons and metastables are comparable for excitation energies in the 10-eV region, although definitive data for such a comparison is unavailable. In any event, this arrangement permitted the observation of metastable excitation with no discernible uv background.

The transit time for the molecules from scattering region to detector was 15 μsec, compared with a mean lifetime for metastable H_2 of 1 msec.[9]

III. RESULTS AND DISCUSSION

A. $B\,^1\Sigma_u^+$ excitation

Figure 3 shows an *XY* recording of the photon excitation function. The energy scale was determined by setting the first resonance peak at 11.30 eV according to a calibration procedure described below. The inset in the figure is a summation of the absolute differential cross sections at 40° for the excitation of the $v = 0, 1, 2$ levels of $B\,^1\Sigma_u^+$ obtained using the energy-loss technique by Weingartshofer *et al.*[4] The identification of our photon data as the excitation function of $B\,^1\Sigma_u^+$ is based on (i) the similarity with the energy-loss data; (ii) a threshold of 11.18 eV which was in good agreement with the spectroscopic value of 11.19 eV for $B\,^1\Sigma_u^+$ to well within the accuracy of our calibration procedure; and (iii) the fact that no other states are known to emit uv photons after excita-

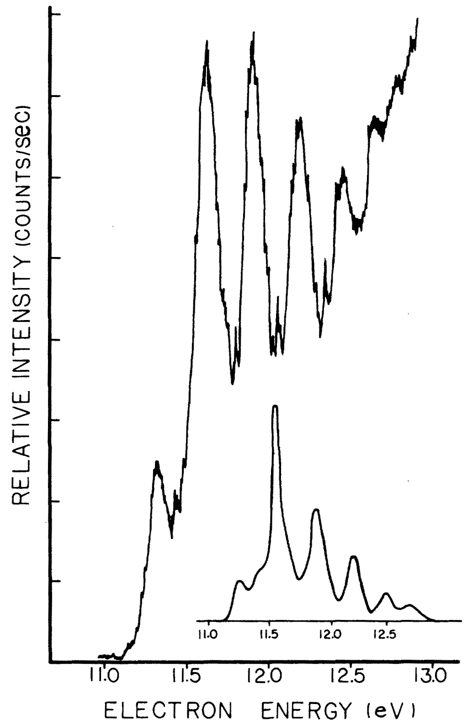

FIG. 3. A direct *XY* recording of the observed $B\,^1\Sigma_u^+$ total excitation function. The inset at lower right, included for comparison, is a summation of the absolute differential cross sections at 40° for the excitation of the $v = 0, 1, 2$ levels of $B\,^1\Sigma_u^+$ obtained by the energy-loss technique (Ref. 4).

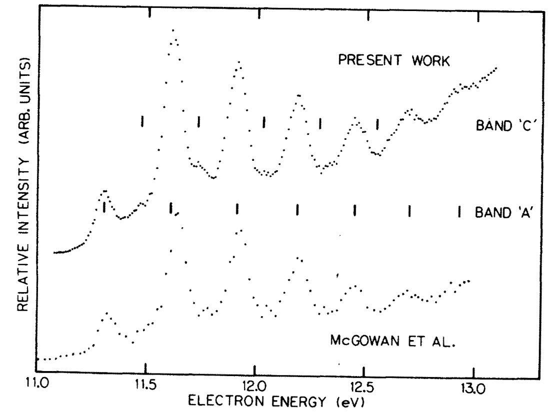

FIG. 4. The total excitation function of $B\,^1\Sigma_u^+$ averaged over six sweeps, (upper diagram), compared with the results of Ref. 6 (lower diagram). The measured positions of the resonances in bands *a* and *c* are indicated by vertical lines.

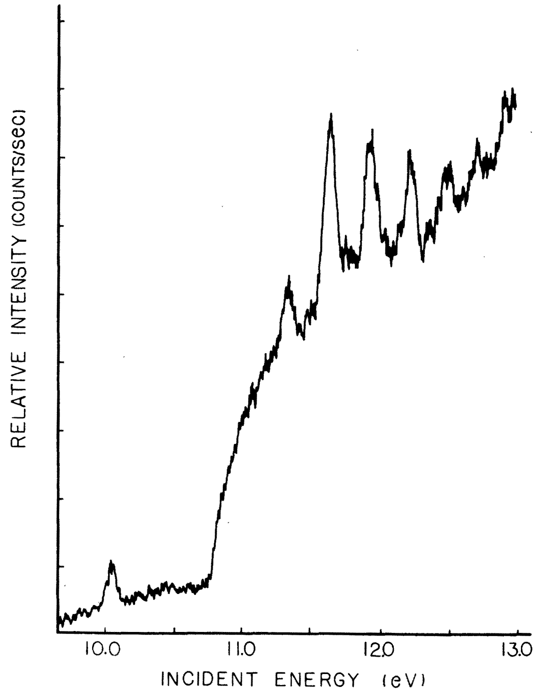

FIG. 5. A direct *XY* recording of the uv excitation function of a mixture of CO and H_2. The isolated peak at 10.04 eV is a resonance in the $A\,^1\Pi$ cross section of CO and was used to calibrate the positions of the resonances in band *a* of H_2 starting at 11.30 eV.

tion by electrons with impact energies below about 12.5 eV. The steep rise in our experimental curve above 12.5 eV is probably due to some higher states. The strongest transitions from the $B\,^1\Sigma_u^+$ ($v=0$) level are to the ground $X\,^1\Sigma_g^+$ ($v=4,5,6$) levels. The corresponding photon energies are about 8.5 eV. In Fig. 4 we compare our data with that of McGowan and Williams, with a corrected energy scale.[6] Their experimental arrangement was similar to ours, except that a methane filter was used to restrict the detector sensitivity to uv photons with energies below 8.8 eV, whereas our sensitivity extended to the cutoff of the MgF_2 window at about 11 eV. This could explain the different background slopes above 12.5 eV.

The energy scale was calibrated by mixing H_2 in the target cell with reference gases whose excitation cross sections exhibit distinct structures at precisely known energies. The structures chosen for calibration were the 10.04-eV resonance in CO,[10] the 10.14-eV resonance at the threshold for excitation of the $4p^5_{3/2}$ ($J=1$) state of krypton,[11] and the peak at 13.08 eV in the total metastable cross section of argon.[12] The first two were chosen because they lie well below the H_2 resonant structures, while the argon feature allowed calibration at the high end of the energy scale.

Figure 5 is an example of calibration data using CO. The target chamber pressures of CO and H_2 were 4.0×10^{-5} Torr and 1.6×10^{-4} Torr, respectively. The 10.04-eV resonance in CO is well separated from a sharp threshold due to both the $B\,^1\Sigma_u^+$ state of H_2 and the $B\,^1\Sigma^+$ state of CO. The principal series of H_2 resonances stands out clearly on the CO background.

The energy calibrations with the three different reference gases showed mutual agreement to within experimental error, typically 0.04 eV for the absolute position of a resonance peak, but the discrepancies between them showed a consistent pattern. The data obtained using CO was assumed to be the most reliable, since the energy scale for this gas has been confirmed by several independent groups, and the excitation curves showed the least interference between features in CO and H_2. The positions of the resonance peaks shown in Table I are based on the CO calibration, and if an average had been taken over the data of all three calibrating gases, they would have been 0.02–0.04 eV higher.

The most prominent peaks in our data (Fig. 4) arise from the vibrational series band *a*. In Table I we compare our data for the positions of these resonances with theory,[3] and with the results of other workers using different techniques. The agreement between the various sets of data, including the corrected uv results of McGowan and Williams, is seen to be excellent. The discrepancies seldom exceed 0.02 eV, and in half of the comparisons the disagreements are no more than 0.01 eV.

The vibrational series of resonances *c* can be seen in Fig. 4 as a set of small peaks between

TABLE I. Comparisons of the energy values for the resonance bands *a* and *c* with the results of other experimental techniques and with theory. The theoretical values for band *a* have been incremented by 0.27 eV as described by Sanche and Schulz, Ref. 13.

Vibrational number (Ref. 1)	Present work		Transmission		Vibrational excitation (Refs. 15, 16)	Energy loss (Ref. 4)	uv excitation (Ref. 6)	Theory (Ref. 3)
	$B\,^1\Sigma_u^+$	$c\,^3\Pi_u$	SS (Ref. 13)	KSM (Ref. 14)				
Band *a*								
0	11.30	Below	11.32	11.28	11.30	11.30	11.32	11.32
1	11.61	threshold	11.62	11.56	11.62	11.62	11.63	11.62
2	11.90	11.90	11.91	11.84	11.91	11.92	11.92	11.91
3	12.19	12.18	12.19	12.11	12.19	12.20	12.20	12.18
4	12.47	12.46	12.44	12.37	12.45	12.46	12.47	12.44
5	12.71	12.70	12.68	12.62	12.68	12.70	12.70	12.68
6	12.93			12.86	12.89	12.93	12.91	
Band *c*								
1	11.46	Below	11.43	11.46	11.50	11.50	11.48	11.46
2	11.72	threshold	11.74	11.72	11.80	11.79	11.78	11.75
3	12.02	12.05	12.03	11.99	12.07	12.08	12.05	12.03
4	12.29	12.33	12.32	12.27		12.38	12.30	12.31
5	12.55	12.59	12.58	12.53				12.58
6			12.83	12.77			12.73	12.84
7			13.06	12.97			12.98	

those of series *a*. Although some of the peaks are barely discernible above noise, they appeared consistently in all our data runs. The intensities of the *c* resonances were typically a factor of 10 smaller than those of neighboring *a* resonances. The positions of the *c* resonances are compared with theory and the results of other experimental techniques in Table I. Agreement with theory,[3] transmission data[13,14] and the corrected results of McGowan and Williams[6] are excellent. The positions of the resonances as obtained by energy loss[4] and vibrational excitation[15,16] lie consistently higher by 0.04–0.09 eV. It has been pointed out by Schulz[1] that there is a problem in understanding the angular distribution in these two cases; furthermore, recent vibrational-excitation experiments[16] have indicated the existence of a lower member of the series at 11.19 eV, which was not observed by the highly sensitive transmission techniques of Sache and Schulz.[13] This energy of 11.19 eV is right at our threshold and a resonance there would have been difficult to identify, although a careful study of the shape of our excitation curve suggests the existence of a resonance at or just below threshold. The vibrational designations of band *c* in Table I have been made on the assumption that the resonance at 11.19 eV constitutes $v = 0$.

B. $c\,{}^3\Pi_u$ excitation

Differential excitation functions for the $c\,{}^3\Pi_u$ state have been observed by the energy-loss technique,[4] but apparently the data was not adequate for the assignment of resonant structure. Figure 6 shows a typical excitation function obtained by us using crossed electron and molecular beams, as described in Sec. II. The data was gathered by sweeping the energy range repeatedly, each energy increment being made in discrete steps. The number of counts at each energy was stored on punched tape. The data shown in Fig. 6 was taken over a period of seven hours and involved six sweeps. The energy scale was calibrated by comparison with known structures in the metastable excitation function of helium.[12] A collimated beam was formed containing a mixture of H_2 and He, and after excitation the metastable states of both species had about the same angles of recoil into the detector. This was because the threshold for helium metastable excitation (19.82 eV) is nearly twice that for molecular hydrogen (11.76 eV), almost compensating for the helium atom being twice as massive. The detector geometry and thermal distribution of velocities in the beams were such that roughly 80% of the metastables of both species had recoil angles that made them detectable. The fact that metastables with very large and very small angles of recoil were not detected had a slight effect on the shape of the experimental excitation curves. This was noticeable when comparing the helium metastable excitation function with that obtained with a target gas cell. The difference was not particularly significant, as shown in Fig. 7, which is a comparison with the gas-cell helium excitation function.

Previous work with an H_2 target cell and a

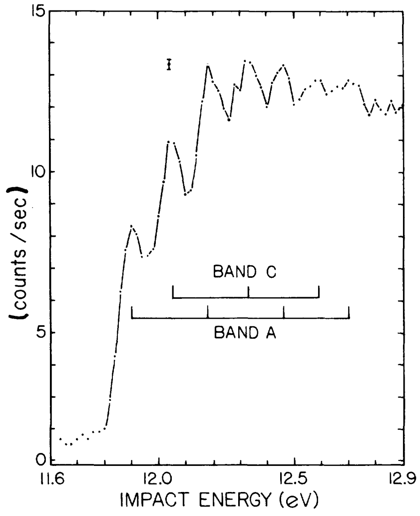

FIG. 6. Excitation function of the $c\,{}^3\Pi_u$ state of H_2 obtained by detecting metastable molecules produced in the electron-molecule crossed-beam mode. The positions of resonance bands *a* and *c* are indicated by vertical lines.

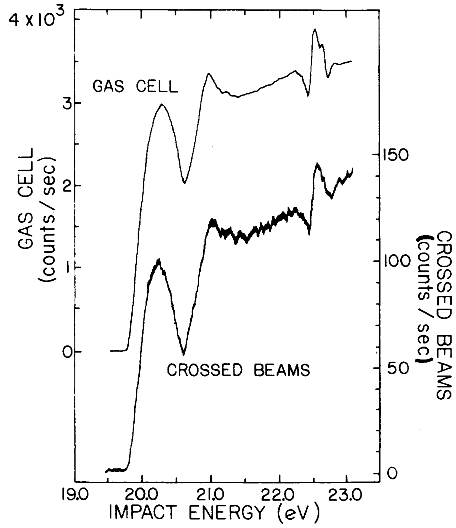

FIG. 7. Comparison of the helium metastable excitation functions using a target gas cell and the crossed-beam configuration.

windowless detector had indicated that metastables and uv photons were detectable in roughly equal amounts after excitation in the range of impact energies 11–13 eV. The enhancement of the metastable signal by the crossed-beam geometry was estimated to be a factor of 80, and hence uv photons after excitation of $B\,^1\Sigma_u^+$ contributed at most 0.2 counts/sec to the data of Fig. 6.

The observed excitation function is identified as the $c\,^3\Pi_u$ state on the basis of good agreement with the currently accepted threshold of 11.76 eV for the $v=0$ vibrational level, and because there is no other known long-lived state in this region of excitation energy. A total of seven resonant peaks are clearly discernible and their measured energy positions are listed in Table I. Four of the values agree to within 0.01 eV of our $B\,^1\Sigma_u^+$ results for members of band *a*, while the remaining three correspond quite closely to results for band *c*. It is apparent, therefore, that these two sets of resonances appear in the $c\,^3\Pi_u$ channel with approximately equal intensities.

Lichten and co-workers[17] have, over a number of years, made a detailed study of the rf spectrum for the $c\,^3\Pi_u$ state using the molecular-beam magnetic-resonance technique. The molecular levels studied in their experiments must be sufficiently metastable to survive for a transit time of the order of 1 msec through their apparatus. Analysis of their data has given a strong indication that two separate vibrational levels are metastable. Their technique does not enable them to identify the particular vibrational levels being observed. The data of Fig. 6 do not give a strong indication of a second metastable threshold (the position of the $v=1$ threshold is at 12.04 eV), but do not preclude its existence with an intensity adequate to explain the rf experiments. We do, nevertheless, confirm that the $v=0$ level is metastable. Time-of-flight measurements have been made of the $c\,^3\Pi_u$ lifetime,[9] but not with unambiguous identification of particular vibrational levels.

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