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Electron impact excitation of H_2 (D_2). Resonance phenomena associated with the X $^2\Sigma_u^+$ and B $^2\Sigma_g^+$ states of H_2^- in the 10 eV region

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Abstract. Quantitative results have been obtained for vibrational excitation of both H_2 and D_2 by electron impact at 10 eV. A strong isotope effect is observed for the lowest levels where the X $^2\Sigma_u^+$ resonance produces the main contribution. The B $^2\Sigma_g^+$ resonance is only observed weakly in the high vibrational level cross sections. Vibrational excitation was also observed at 5 eV where only the X $^2\Sigma_u^+$ resonance is present.

The near-threshold cross section of the b $^3\Sigma_u^+$ state was determined with the aim of observing the B $^2\Sigma_g^+$ resonance in this channel. No such contribution was detected, the cross section appeared to be dominated by direct scattering.

1. Introduction

It is now well established since the first calculations by Bardsley *et al* (1966) that two negative ion states are responsible for all the resonant phenomena occurring in electron scattering on H_2 below 11 eV. The first and ground state of the H_2^- ion is the X $^2\Sigma_u^+(1s\sigma_g)^2 2p\sigma_u$ state and the second is the B $^2\Sigma_g^+ 1s\sigma_g(2p\sigma_u)^2$ state, both dissociating to a ground-state H atom and H^- ion (figure 1).

The $^2\Sigma_u^+$ state has been calculated by Bardsley and Wadehra (1979) and McCurdy and Mowrey (1982) to lie at about 2 eV with a very large width of the order of 10 eV. There is some debate whether a resonance with such a short lifetime can be called a resonance. However from an experimental point of view the angular behaviour of the scattered electrons shows a pσ behaviour which is compatible with a X $^2\Sigma_u^+$ shape resonance with the electron trapped inside a centrifugal barrier. Also this resonance would be responsible for the dissociative attachment phenomena occurring at the dissociation threshold (e.g. Allan and Wong 1978).

The repulsive B $^2\Sigma_g^+$ state lies about 10 eV above the ground-state minimum of H_2. The most recent calculations of Buckley and Bottcher (1977) and Bardsley and Cohen (1978) put this resonance in the class of core-excited shape resonances in the Franck–Condon region and locate its potential curve about 1 eV above its b $^3\Sigma_u^+$ state parent. Recent experiments would locate the B state of H_2^- about 0.8 eV above its parent (Esaulov 1980) and its width in the Franck–Condon region would be about 2 eV (Bardsley and Wadehra 1979) which is determined essentially by the coupling to its

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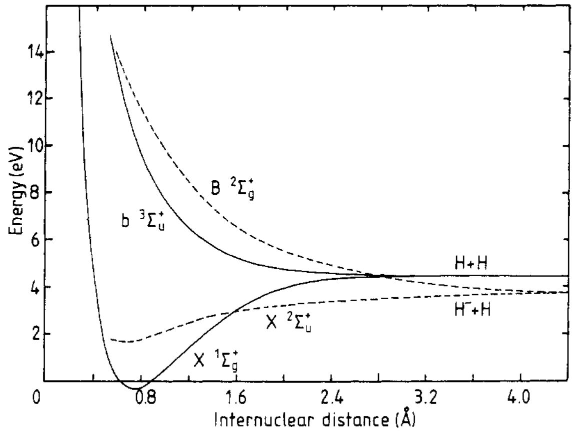

Figure 1. Potential curves for the lowest two states of H_2 (full curves) and H_2^- (broken curves). The X-state curve of H_2^- is based on the calculations of McCurdy and Mowrey (1982) normalised to the H_2 curve at 1.6 Å and that of the B state is based on those of Bardsley and Cohen (1978).

parent. The B $^2\Sigma_u^+$ state is responsible for H^- formation by dissociative attachment and Tronc *et al* (1977) observed the angular dependence of these ions and interpreted the results in terms of contributing sσ and dσ waves whose intensity ratio was 1 : 1.2 at 10 eV.

Bardsley and Wadehra (1979) by means of the semi-empirical local complex potential model have attempted to give a comprehensive account of all the resonant phenomena occurring below 11 eV. These calculations indicate that vibrational excitation is dominated throughout this energy region by the X $^2\Sigma_u^+$ resonance and that the B $^2\Sigma_g^+$ resonance only plays an important role in excitation of high vibrational levels.

In previous publications (Gresteau *et al* 1977, Hall 1977) we reported the observation of the B resonance in high vibrational levels of the H_2 and D_2 ground states. Here we present quantitative results at 10 eV for vibrational excitation of both isotopes which show the varying contributions of both resonances. Results at 5 eV are also presented.

We have also determined the b $^3\Sigma_u^+$ excitation cross section in the threshold region where the B $^2\Sigma_g^+$ resonance is predicted to be present.

2. Experimental method

The observations were performed with an electron impact spectrometer which has been presented in detail previously (Gresteau *at al* 1979). Cylindrical 127° electrostatic filters are employed, firstly to produce a narrow energy spread electron beam and secondly to analyse the energy and angle of the electrons scattered from the incident beam by the target molecules effusing from a small tube. The apparatus is characterised by a very high sensitivity which is attained by using two filters in tandem for the post-collision analysis and housing the spectrometer elements in differentially pumped chambers. In this way signal count rates down to a few counts/min can be detected corresponding to processes with cross sections as low as 10^{-21} cm^2.

3. Results

3.1. Ground-state excitation

Preliminary observations made in this laboratory (Gresteau *et al* 1977, Hall 1977) showed that the B $^2\Sigma_g^+$ resonance leads to detectable excitation of all vibrational levels. The demonstration of the appearance of this resonance in the differential cross sections for vibrational excitation can be seen in figure 2. The main contribution to the $v = 1$ cross section comes from the X $^2\Sigma_u^+$ resonance but as the vibrational level increases the B $^2\Sigma_g^+$ resonance shows up more strongly until $v = 5$ where it represents the dominant contribution to the cross section at this 140° scattering angle. Some deformation of these curves is introduced by the electron optics but this affects neither the overall forms of the curves nor the observed evolution. The broken part of the curve is a rough-hand extrapolation of the cross section through a region where much sharp structure is present due to well known Feshbach resonances (Comer and Read 1971). The sharp Feshbach resonances can be seen in detail in figure 3 and the prominent sequence known as series 'a' was used to calibrate the incident energy scale (Joyez *et al* 1973). The figure also shows the B-state resonance as it appears in the $v = 4$ channel at 140°. The broken curve is normalised to the experimental results at 9.8 eV and represents the Franck–Condon envelope for b $^3\Sigma_u^+$ state excitation from the ground-state $v = 0$ level. This envelope was obtained experimentally by recording an energy-loss spectrum with a fixed residual energy of 10 eV at a 140° angle. At this residual energy the incident energy is scanned between 17 and 22 eV and the observed b-state envelope can be considered free from instrumental effects, particularly those produced by the chromaticity of the electron optics. This Franck–Condon envelope is very similar to that given by Rescigno *et al* (1976). The difference between the broken curve and the

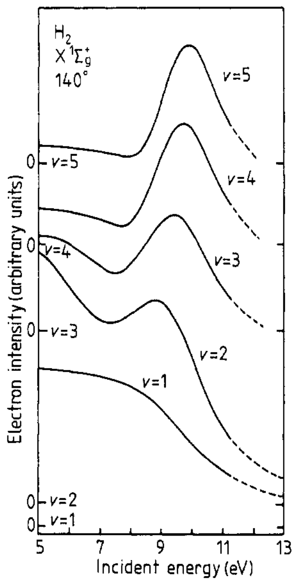

Figure 2. Differential cross sections for excitation of the indicated vibrational levels of the H_2 X $^1\Sigma_g^+$ ground state at a 140° scattering angle. The zero level for each curve is also indicated. The curves are not to scale.

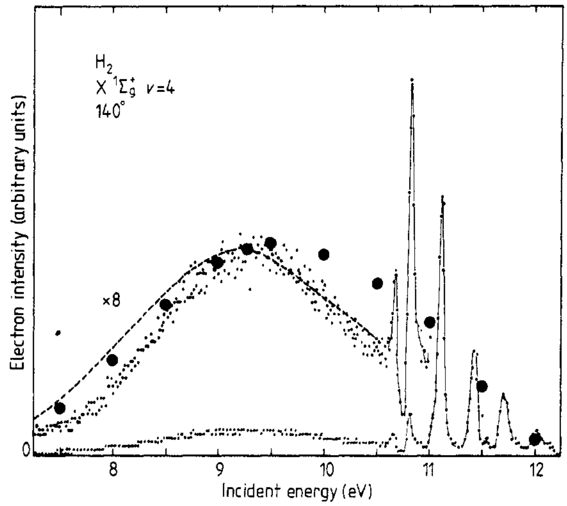

Figure 3. Differential cross section for excitation of the $v = 4$ level of the H_2 ground state at 140°. The broken curve is the observed Franck–Condon envelope for b $^3\Sigma_u^+$ state excitation and the full circles represent the H^- formation cross section derived from the measurements of Rapp *et al* (1965). The curves are normalised together at 9.8 eV.

excitation function of $v = 4$ is probably not significant given the experimental uncertainties in the latter. The difference is not sufficiently large to give information on the position of the B $^2\Sigma_g^+$ state potential curve of H_2^- relative to that of the b $^3\Sigma_u^+$ state of H_2 other than that they are close together which is well known. The full circles represent the cross section for dissociative attachment measured by Rapp *et al* (1965), allowance being made for the presence in their results of a linear rising background. It was found in previous observations on H^- formation in H_2 performed in this laboratory (Tronc *et al* 1977) that the cross section falls to about zero just below the 14 eV process whereas Rapp *et al* (1965) at this point observed a H^- intensity about 40% of that detected at 10 eV. Note that on the high-energy side of the broad peak, the dissociative attachment results fall off more slowly than the other two sets of observations.

Energy loss spectra recorded at 10 eV and 140° for both H_2 and D_2 are presented in figure 4 on a semi-log scale. This demonstrates that the resonant processes lead to observable excitation of all discrete vibrational levels as well as to excitation of the nuclear continuum in both isotopes. For intensity reasons the energy resolution is low (~70 meV) thus no rotational structure is apparent.

The differential cross sections for exciting the first five vibrational levels of H_2 and the first level of D_2 at 10 eV are shown in figure 5. These results were obtained from energy loss spectra at different angles and subsequent normalisation of the relative intensities to the absolute differential elastic cross section of H_2. The elastic cross section was obtained from the H_2 to He relative elastic cross sections of Srivastava *et al* (1975) normalised to the absolute helium cross sections of Andrick and Bitsch (1975). In evaluating the relative peak intensities the integral was taken thus allowing for rotational structure. Differential cross sections for higher levels were not measured due to lack of intensity.

The lower full curve is the theoretical angular dependence expected for the B $^2\Sigma_g^+$ resonant state normalised to experiment at 90° taking into account s and d partial

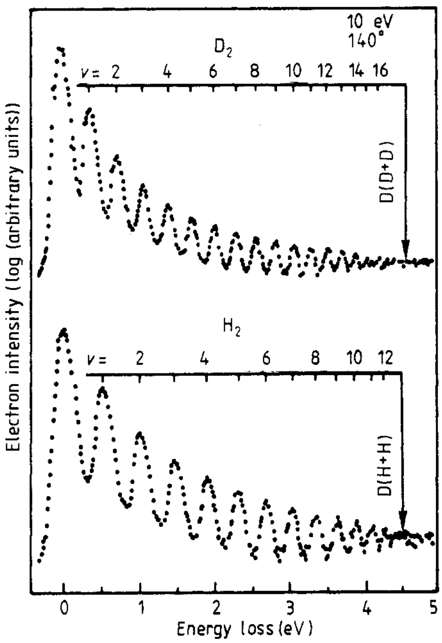

Figure 4. Energy loss spectra for H_2 and D_2 at 10 eV and 140° on a semi-log scale.

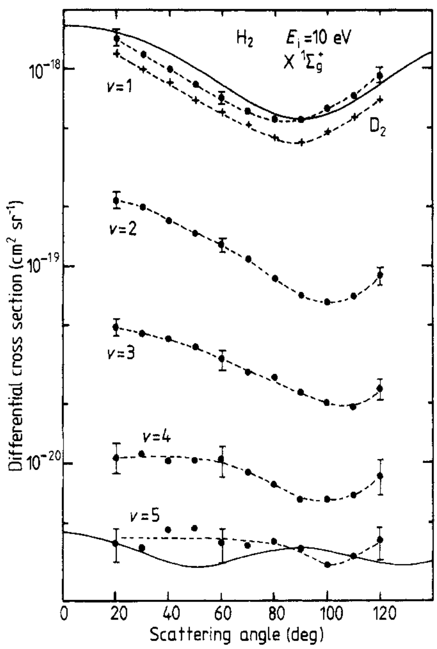

Figure 5. Differential cross sections for vibrational excitation of the H_2 and D_2 ground states at 10 eV. The full curves represent theoretical angular dependences.

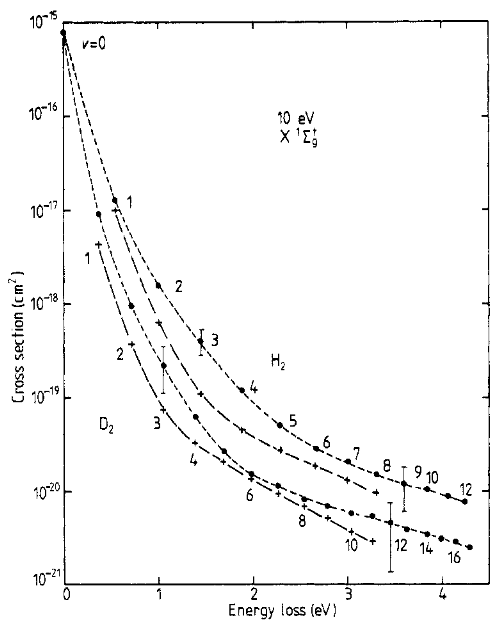

Figure 6. Integral cross sections for vibrational excitation of the H_2 and D_2 ground states at 10 eV (full circles). The crosses represent the theoretical results of Bardsley and Wadehra (1979).

waves and their relative intensities determined by Tronc *et al* (1977) and using the theory of Fiquet-Fayard (1975). In this case exactly the same angular behaviour was obtained using the theory of Andrick and Read (1971). The upper full curve is the theoretical angular dependence for the X $^2\Sigma_u^+$ resonance and a pσ partial wave ($1 + 2\cos^2\theta$). Note that for the case of an isolated resonance in homonuclear diatomic molecules integrated over rotational channels the differential cross section is always symmetrical with respect to 90°.

The integral cross sections for vibrational excitation at 10 eV (figure 6) were evaluated from the differential cross sections of figure 4 for $v \leq 5$. The values for $v > 5$ were obtained by normalising the differential relative intensities seen in energy loss spectra at 140° to the integral value of $v = 5$. As the differential cross section form is expected to evolve to the theoretical form this would introduce some error. We estimate that the error is about ±30% up to $v = 5$ increasing to at least ±50% for the highest levels. For these levels the cross section is probably overestimated due to some focusing of the electron optics at these high energy losses.

The errors for D_2 are somewhat larger as only the differential cross section for $v = 1$ was determined; again by normalisation to the elastic cross section assuming that it is identical to that of H_2. The integral cross sections of the other levels were then obtained from the relative intensities at 140° normalised to the $v = 1$ integral cross section with an estimation being made for the evolving angular dependencies by referring to those of H_2. Figure 6 also shows the theoretical cross sections of Bardsley and Wadhera (1979).

Differential cross sections were also obtained at 5 eV for the $v = 1$ level for both isotopes and are shown in figure 7 along with the theoretical form for a Σ_u^+ resonance ($1 + 2\cos^2\theta$). Integral cross sections were then evaluated and the results are shown in figure 8. The experimental procedure was identical to that used at 10 eV. The error here rises from about ±30% for $v = 1$ to ±80% for the highest levels measured as the focusing effects at this energy are more critical. The theoretical results of Bardsley and Wadehra (1979) are also presented in figure 8.

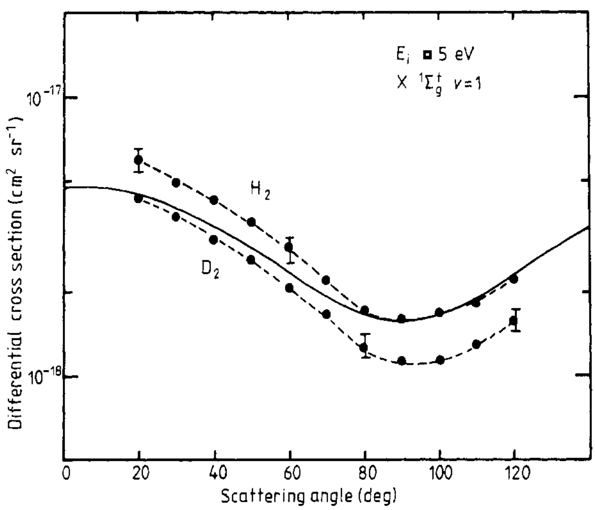

Figure 7. Differential cross sections for excitation of the $v = 1$ level of the H_2 and D_2 ground states at 5 eV. The full curve represents a theoretical angular behaviour.

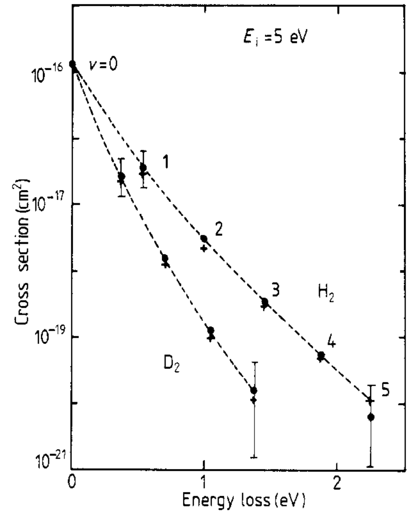

Figure 8. Integral cross sections for vibrational excitation of the H_2 and D_2 ground states at 5 eV (full cirles). The crosses represent the theoretical results of Bardsley and Wadehra (1979).

3.2. *Excitation of the b $^3\Sigma_u^+$ state*

The b $^3\Sigma_u^+$ cross sections were obtained in the following way. First a series of excitation functions was obtained from 0.2 to 2.2 eV above threshold at different angles for an energy loss of 10 eV which corresponds to b-state excitation in about the middle of the Franck–Condon region. These were then corrected for instrumental effects by normalisation to the angular and energy distribution of electrons resulting from the ionisation process 2.2 eV above threshold (Pichou *et al* 1978). It was assumed that the results of Pichou *et al* (1978) which were obtained for He were also true for H_2, although this is expected to be so it remains to be demonstrated. The corrected excitation functions indicated that the differential b-state cross section was flat to a good approximation between 0.2 and 2.2 eV above threshold at all angles (10° intervals from 20° to 120°) and rose quite steeply with increasing angle.

The excitation functions were put on an absolute cross section scale by normalisation to the 2^3S cross section of He at 90° and 1.6 eV above the threshold of Pichou *et al* (1976). The two gases were mixed together during the measurements and their relative densities were obtained from the elastic He to H_2 cross section ratios of Srivastava *et al* (1975). The H_2 contribution to the elastic peak was determined from the intensity of the $v = 1$ peak (integral), having previously measured the $v = 1$ to elastic peak ratio in the absence of He. Account was taken of the instrumental resolution as the measured intensity of the b state which is a continuum process depends on it. At the same time the b-state angular behaviour at $\Delta E = 10$ and 1.6 eV above threshold was verified against that of the 2^3S cross section and essentially the same dependence was obtained as that determined using the ionisation process in H_2 as a calibration standard. The resulting differential cross sections for b-state excitation for $\Delta E = 10$ and 10.5 eV incident energy (i.e. 0.5 eV above threshold) are shown in figure 9. The smooth curve is the angular behaviour obtained using the theory of Fiquet-Fayard (1975) with s and p waves in the entrance channel, the relative intensities given by Tronc *et al* (1977) and a p wave in the exit channel. This curve is arbitrarily normalised to 1×10^{-18} cm^2 sr^{-1} eV^{-1} at 40°.

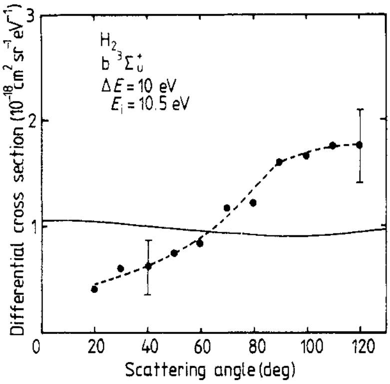

Figure 9. Differential cross section for excitation of the b $^3\Sigma_u^+$ state of H_2 at 10.5 eV for a 10 eV energy loss, i.e. 0.5 eV above threshold. The smooth curve is a theoretical resonant angular dependence (see text).

The differential cross sections for b-state excitation at 10.5, 11.0, 11.6 and 12 eV were then obtained by integrating over the accessible Franck–Condon region and assuming that the differential b-state cross sections were independent of energy loss as was indicated by the flat excitation functions. The results obtained at 12 eV are shown in figure 10 from 20° to 120°. We would estimate the error to be at least ±25% not including an uncertainty in the He cross section which Pichou *et al* (1976) gave as ±30%. Also shown in figure 10 are the theoretical results of Fliflet and McKoy (1980).

The differential cross sections were extrapolated to 0 and 180° and integrated to give the total cross sections for b-state excitation at four energies. The results are shown in figure 11 and the error here would be at least ±40%. Also presented in the figure are the calculated values of Fliflet and McKoy (1980) and the experimental values of Corrigan (1965) who observed H-atom formation.

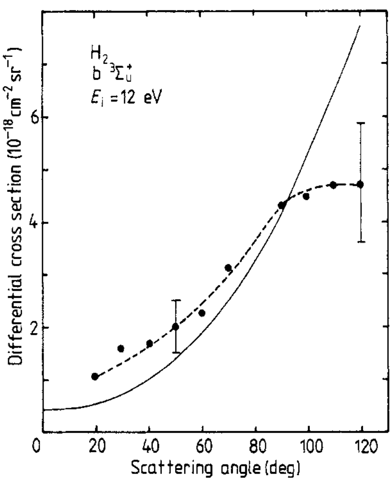

Figure 10. Differential cross section for excitation of the b $^3\Sigma_u^+$ state of H_2 at 12 eV. The smooth curve represents the theoretical results of Fliflet and McKoy (1980).

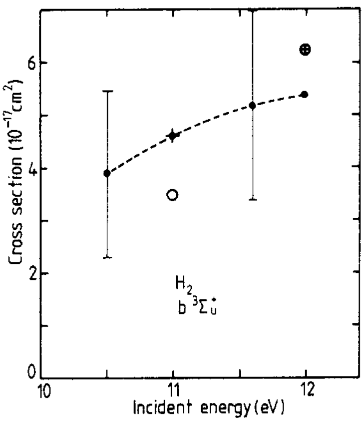

Figure 11. Integral cross section for excitation of the b $^3\Sigma_u^+$ state of H_2 (full circles). Crosses are the values of Fliflet and McKoy (1980). Open circles are the experimental results of Corrigan (1965).

4. Discussion

At 5 eV the only resonance contributing to vibrational excitation is the short lived and very broad X $^2\Sigma_u^+$ resonance. This resonance has essentially only a pσ contributing partial wave as is shown by the angular behaviours of the differential cross sections (figure 7) which have a dependence similar to the $(1+2\cos^2\theta)$ dependence expected for this partial wave. The short lifetime of this resonance is reflected in the fast decrease in the vibrational cross sections (figure 8) with increasing vibrational energy, this decrease being about linear on the semi-log scale. Note the good agreement between these measurements and the calculated values of Bardsley and Wadehra (1979).

At 10 eV the $^2\Sigma_u^+$ resonance is still the main contributor to excitation of the $v=1$ level as is borne out by the differential cross section behaviour (figure 5) which is very similar to that at 5 eV (and to $1+2\cos^2\theta$). The B $^2\Sigma_g^+$ resonance is only detectable for the $v=2$ and higher levels (figure 2). The presence of this resonance which has a much longer lifetime reduces the rate at which the vibrational cross sections decrease. For low levels adjacent levels decrease by nearly a factor of ten whereas for the high levels this factor is near one. In the calculation of Bardsley and Wadehra (1979) the contribution of each resonance consists, on the semi-log scale, of an almost straight line which is steep for the $^2\Sigma_u^+$ state and almost flat for the $^2\Sigma_g^+$ state. These two contributions added together give the smooth curves of decreasing slope shown in figure 6. This being so then it would appear that the calculated values for H_2 reach the linear part corresponding to the B $^2\Sigma_g^+$ contribution for lower levels than do the observed values, i.e. approximately $v=4$ for theory and approximately $v=6$ or 7 for experiment. The same would occur for the D_2 molecule and would indicate that theory underestimates the contribution of the X $^2\Sigma_u^+$ resonance at 10 eV. Note that the X $^2\Sigma_u^+$ contribution falls off more rapidly for D_2 than for H_2 which is what one would expect for a resonance with a very short lifetime. On the other hand the more long lived B $^2\Sigma_g^+$ resonance produces a less noticeable isotope effect in the region where decay to the high levels occurs and the cross section curves are about parallel.

The interplay of the X $^2\Sigma_u^+$ and B $^2\Sigma_g^+$ resonances leads to the evolving differential cross sections of figure 5. The angular dependence becomes flatter as v increases but for $v = 5$, the highest level we were able to measure, still has not attained the theoretical form if this is to be the true physical form. What is more the curve of the $v = 5$ level is asymmetrical with respect to 90° as also are those of $v = 2$, 3 and 4, which is theoretically not possible for a single resonance and can only take place if interference occurs between two resonances. We have examined the interference terms in the theory of Andrick and Read (1971) for the Σ_u^+ and Σ_g^+ resonances and for the above-mentioned partial waves. These terms vary as either $\cos\theta$ or $\cos^3\theta$ and can thus produce the observed angular asymmetry. This would thus indicate that the $^2\Sigma_u^+$ resonance still contributes to the $v = 5$ cross section at 10 eV. The calculation of Bardsley and Wadehra (1979) indicates that the $^2\Sigma_u^+$ contribution is small here; less than 5% that of the $^2\Sigma_g^+$ state.

The intention in studying the near threshold excitation of the b $^3\Sigma_u^+$ state was to observe decay of the $^2\Sigma_g^+$ resonance into what would be its parent state. Firstly, the angular behaviour shown in figure 9 taken where the resonance should be strong does not have forward–backward symmetry and is very different from the theoretical form. Secondly, the differential cross section at 12 eV is similar both in form and magnitude to that calculated by Fliflet and McKoy (1980). This calculation only considers direct excitation processes and cannot describe reactions which proceed via a resonance. Thus it seems that the resonant contribution, if it is present, is overshadowed by direct processes. Similarly, although this is less demonstrative, the integral cross section shown in figure 1 does not have a form one would expect for the B-state resonance. This should be something like the Franck–Condon envelope of the b state of H_2, i.e. showing a maximum near 9 eV and falling to zero by about 12.5 eV.

Finally, we should point out the slower fall off to the dissociative attachment cross section compared with the vibrational excitation function (figure 3). This would not appear to be due simply to a contribution from Feshbach resonances to the H^- yield (see Tronc *et al* 1977) and would thus reflect an increased survival probability of the resonance to dissociation as the incident energy increases, i.e. as the resonance is formed higher up the potential curve.

5. Conclusion

Our goal in this study was to make quantitative observations of the decay of the B $^2\Sigma_g^+$ resonance to its two open channels, i.e. to the ground state of H_2 (D_2) and to its parent b $^2\Sigma_u^+$ state. Cross sections were obtained for vibrational excitation of nearly all levels at 10 eV for the two isotopes. Their cross sections reveal a strong isotope effect for the X $^2\Sigma_u^+$ resonance which contributes strongly to the first levels, but this effect is almost absent for the B $^2\Sigma_g^+$ state which is observed mainly in the higher levels. This behaviour is what one would expect considering the very different resonance lifetimes. Although short lived the X $^2\Sigma_u^+$ resonance still produces noticeable excitation of the $v = 5$ level of H_2 as the asymmetry of the angular behaviour showed. This would not be expected from the calculations of Bardsley and Wadehra (1979). The results of these authors, however, are in good agreement with our observations of vibrational excitation at 5 eV.

The observations in the b $^3\Sigma_u^+$ state channel from threshold to about 2 eV above did not clearly reveal any resonant phenomena. These, if present, appeared to be masked by direct scattering. However, the measured cross sections were in good agreement with the calculations of Fliflet and McKoy (1980) whose technique could not reproduce resonant effects.

Acknowledgments

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