

LETTER TO THE EDITOR

***Ab initio* cross sections for the excitation of the $b^3\Sigma_u^+$ state of H_2 by electron impact in the distorted-wave approximation†**

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Abstract. We present differential cross sections for the $x^1\Sigma_g \rightarrow b^3\Sigma_u$ transition in H_2 at 15 eV incident electron energy. The cross sections are computed in the distorted-wave approximation, using the random-phase approximation for the electronic transition density and a discrete basis set technique for obtaining the distorted waves. Our cross sections are found to be in good agreement with experimental data.

This letter describes our first results on the electronically inelastic, low-energy, electron-molecule scattering problem. We present *ab initio* cross sections for the excitation of the $b^3\Sigma_u$ state of H_2 by electron impact. The results we report are for an incident electron energy of 15 eV. To our knowledge this is the first calculation of an electronically inelastic electron-molecule differential scattering cross section that goes beyond the high-energy approximations of the Born or eikonal type||. We find good agreement with the previously unpublished experimental results of Srivastava and Trajmar (1975), whereas the Born approximation at this energy fails badly.

We have assumed the validity of the Born-Oppenheimer approximation in separating the electronic and nuclear portions of the scattering wavefunction. The rotational motion was treated in the usual adiabatic approximation (Temkin and Vasavada 1967) which allows one to calculate the electronic part of the transition matrix in the body-fixed frame of the molecule and then average the cross section, at a given scattering angle, over all orientations of the molecule with respect to a laboratory-fixed frame. Furthermore, we make a Franck-Condon approximation for the vibrational contribution to the cross section, by assuming that the electronic contribution to the transition matrix is independent of the internuclear separation (over the small region where the overlap of the initial and final nuclear vibrational wavefunctions $S_{v,v'}$ is non-zero). With these assumptions, the cross section for the excitation of a particular electronic/vibrational

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|| Approximate values of the total cross section for exciting the $b^3\Sigma_u$ state of H_2 were computed in 1958 by L A Edelstein *Nature, Lond.* **182** 932. Details of the calculation were not given, although some discussion of this work can be found in H S W Massey 1969 *Electronic and Ionic Impact Phenomena* vol 2 (Oxford: Pergamon) p 894.

state is given by

$$\sigma(k_f, v' \leftarrow k_i, v) = \frac{k_f}{k_i} \frac{1}{4\pi^2} S_{v'v} \frac{1}{4\pi} \int d\Omega |T_{fi}^{el}|^2 \quad (1)$$

where the integral is over all orientations of the molecule and k_i and k_f , the initial and final momenta, are given by

$$\frac{1}{2}k_i^2 = \Delta E_{fi} + \frac{1}{2}k_f^2 \quad (2)$$

and ΔE_{fi} is the excitation energy between the initial and final electronic/vibrational states. For the electronic transition energy, we used the value given by Kolos and Wolniewicz (1965) at the equilibrium internuclear separation of $1.4 a_0$.

In the present calculation we employ the distorted-wave approximation for the electronic transition matrix, using the ground-state Hartree–Fock potential as the distorting potential and the random-phase approximation (RPA) for the electronic transition densities. This approximation is described at length elsewhere (Rescigno *et al* (1974c), and allows us to write the transition matrix element T_{fi}^{el} in the particularly simple form,

$$T_{fi}^{el} = \sum_{m,\alpha} U_{m\alpha} Y_{m\alpha}^*(f) + U_{\alpha m} Z_{m\alpha}(f) \quad (3)$$

where $Y_{m\alpha}(f)$ and $Z_{m\alpha}(f)$ are RPA amplitudes and $U_{m\alpha}$ is defined by

$$U_{m\alpha} = \int d^3r d^3r' \phi_m^*(r) \phi_{k_f}^{(-)}(r)^* \frac{1}{|r-r'|} \phi_\alpha(r) \phi_{k_i}^{(+)}(r') - \text{exchange}. \quad (4)$$

In equation (4) ϕ_m is an unoccupied Hartree–Fock spin orbital and ϕ_α is the occupied σ_g spin orbital of H_2 . The distorted waves $\phi_{k_i}^{(+)}$ and $\phi_{k_f}^{(-)}$ are Hartree–Fock continuum spin orbitals with incoming (+) and outgoing (–) boundary conditions. The particular form of the distorted-wave approximation we are using, in which both continuum orbitals are computed in the field of the initial state, was explicitly derived by Csanak *et al* (1971) and successfully applied to electron–helium scattering (Thomas *et al* 1974). Similar results for e–He were obtained by Madison and Shelton (1973) and, more recently, Pindzola and Kelly (1975) obtained good values for the electron excitation cross sections of the 2S and 2P states of H using this form of the distorted-wave approximation.

In computing $\phi_k^{(\pm)}$ we make use of an expansion technique using square-integrable basis functions developed previously by the authors (Rescigno *et al* 1974a, b) and applied to elastic electron– H_2 scattering (Rescigno *et al* 1975). In this approach the Lippman–Schwinger equation for $\phi_k^{(\pm)}$ is reduced to a finite matrix problem by expanding the ground-state Hartree–Fock potential in a finite set of two-centre Gaussian functions, $\varphi_\alpha(r)$,

$$\phi_k^\pm(r) = \sum_\alpha \varphi_\alpha(r) C_\alpha(\mathbf{k}), \quad (5a)$$

$$C_\alpha(\mathbf{k}) = \langle \alpha | \mathbf{k} \rangle + \sum_{\beta,\gamma} G_{\alpha\beta}^0 V_{\beta\gamma} C_\gamma(\mathbf{k}). \quad (5b)$$

This is an important simplification, since it allows us to avoid one-centre expansions and/or numerical integration of the Schrödinger equation for the distorted waves in the presence of a non-spherical potential.

The electronic transition matrix elements were then computed so as to compensate for the fact that a truncated basis set representation of ϕ_k^\pm was used. Since the first

term in ϕ_k^\pm (equation (5b)) is simply a plane wave, $U_{m\alpha}$ (equation (4)) will contain a plane-wave contribution which we can write as

$$U_{m\alpha}^{\text{Born}} = \left\langle mk_f \left| \frac{1}{r_{12}} \right| \alpha k_i \right\rangle - \text{exchange.} \quad (6)$$

The basis set representation of $U_{m\alpha}^{\text{Born}}$ was thus subtracted from $U_{m\alpha}$ and replaced by the exact plane-wave matrix element. This substitution also includes the Born contributions from the higher symmetry types not included in the basis (Rescigno *et al* 1974b).

The basis set used to generate the RPA amplitudes (equation (3)) consisted of a [10s/5p] set of primitive Gaussians on each centre. The distorted-wave basis, which must contain a significant number of diffuse functions in order to represent the tails of the continuum orbitals, consisted of a set of [20s/7z/15x/15y] Gaussians on each centre, whose exponents were chosen in a geometric series. With this basis, the Σ_g , Σ_u , Π_g and Π_u contributions to the electronic amplitude could be constructed; other symmetries were included only to the extent that they contributed to the exact Born terms of equation (6).

The results we are reporting are for the excitation of the total vibrational band corresponding to the $b^3\Sigma_u$ electronic state of H_2 ; that is, the cross section from equation (1) is summed over all final states v' . Since the $b^3\Sigma_u$ state is dissociative, the Franck-Condon factor involves the overlap of a bound and a continuum nuclear vibrational function. This overlap was evaluated by numerical quadrature, using a harmonic oscillator initial state with parameters taken from Herzberg (1950), and a final vibrational wavefunction that was generated numerically, using the $b^3\Sigma_u$ potential energy curve of Kolos and Wolniewicz (1965) and a Runge-Kutta integration scheme. Our computed Franck-Condon curve was found to be in good agreement with the shape of the observed dissociative feature in the electron-impact energy-loss spectrum (Srivastava

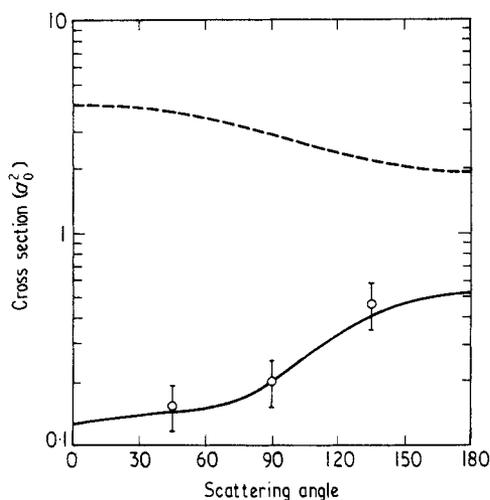


Figure 1. Differential cross section for the excitation of the $b^3\Sigma_u$ state of H_2 by 15 eV incident electrons. Numerical results using the distorted-wave approximation (full curve) are compared with normalized experiment and with the results obtained in the Born approximation (broken curve). Cross sections are for excitation of the entire vibrational band and are given in atomic units.

and Trajmar 1975) and was thus used to extend the latter feature for the purpose of computing the total area under the dissociative curve, which should be proportional to the total cross section we evaluated.

The results of our computation are shown in figure 1 along with the previously unpublished results of Srivastava and Trajmar (1975). The latter relative figures have been normalized to our values at 90° . The agreement of our computed differential cross section with experiment is seen to be good. We have also plotted the plane-wave approximation obtained by setting $U_{mx} = U_{mx}^{\text{Born}}$; this is frequently referred to (Truhlar *et al* 1968) as the Born–Oppenheimer minus core approximation (BOMC). In contrast to the full distorted-wave approximation, the BOMC fails badly at this low incident electron energy of 15 eV. Absolute total cross sections for the dissociation of H_2 by electron impact have been measured by Corrigan (1965). Our value for the integrated cross section at 15 eV is $0.994 \pi a_0^2$. This number is consistent with Corrigan's observed value of 0.98 for the total cross section for dissociation of H_2 by 15 eV electrons, and this supports the supposition that the low-energy electron-impact dissociation of H_2 proceeds mainly through direct excitation of the $b^3\Sigma_u$ state (Cartwright and Kuppermann 1967, Trajmar *et al* 1968).

The preliminary results we have obtained for $x^1\Sigma_g \rightarrow b^3\Sigma_u$ transition in H_2 at 15 eV are very encouraging. Further calculations at other incident electron energies and for different electronic states are under way and will be described in a future publication. Cross sections for the excitation of the $a^3\Sigma_g$ state, which will also lead to dissociation of H_2 following a transition to the $b^3\Sigma_u$ state, will be required before comparison with Corrigan's data can be made reliably.

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