

Resonances in the Electronic Excitation of Molecular Hydrogen

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Ab initio R -matrix scattering calculations are presented for electron- H_2 collisions for energies up to 30 eV. Excitation from the ground state, $X^1\Sigma_g^+$, to five accurately represented, low-lying electronic states, $b^3\Sigma_u^+$, $a^3\Sigma_g^+$, $B^1\Sigma_u^+$, $c^3\Pi_u$, and $C^1\Pi_u$, is explicitly considered. An attempt is made to rationalize the wealth of experimental data. Resonance structures similar to those assigned experimentally to the a and c series are found as well as a number of other resonancelike features.

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The scattering of electrons by molecular hydrogen is one of the most fundamental processes in the field of molecular physics. Despite this there are many areas of uncertainty concerning a range of processes including electronic excitation, dissociative recombination, and differential cross sections.¹ In particular, even for this apparently simple system, theoretical calculations on the electronic-excitation process have been restricted to two states (see, for instance, Refs. 2–7). All of these studies used single-configuration wave functions to represent the electronic states involved.

Hydrogen, in common with most molecules, has a number of nearby low-lying electronic states. In particular, there are experimental data on excitation to the lowest excited states,^{8–14} all of which have vertical excitation thresholds in the range 10–13 eV. These studies yield a wealth of data including features which have been associated with several series of resonances.^{8,10,15} Theoretically these resonances have been studied using nonscattering (Feshbach or stabilization) techniques.^{16–18} However, despite these, the exact provenance of the resonances is still controversial¹⁰ and many questions remain to be answered on the electronic-excitation cross sections.¹

Clearly, a thorough theoretical treatment of low-energy electronic-excitation processes in H_2 must take account of the low-lying states. To do this successfully, it is also necessary to have accurate electronic-excitation thresholds for each state included in the calculation. This cannot be achieved by using simple single-configuration wave functions.

In this Letter we report electronic-excitation calculations on H_2 using up to six states in the close-coupled expansion. These calculations are performed using a target basis optimized to give a good representation of all the target states involved. These states were calculated using a full-configuration interaction within the basis of Slater-type orbitals (STO's) specified below. To our knowledge this is the first time a sophisticated and reliable target wave function has been used to study the electron-impact electronic excitation of any molecule.

Target representations were obtained in the following

manner. The σ_g orbitals were taken as those optimized by Fraga and Ransil¹⁹ for the $X^1\Sigma_g^+$ ground state. This $(1s, 2s, 2p_\sigma)$ set has exponents 1.378, 1.176, and 1.820, respectively. The σ_u -orbital exponents were optimized for a self-consistent-field (SCF) calculation on the lowest state of $^1\Sigma_u^+$ symmetry giving 1.081, 0.800, and 1.820, respectively, for a $(1s, 2s, 2p_\sigma)$ set. A set of π_u orbitals were obtained by optimizing a $(2p_\pi, 3p_\pi, 3d_\pi)$ set for an SCF calculation on the lowest $^1\Pi_u$ state giving exponents 0.574, 0.636, and 1.511, respectively. Finally, the π_g orbitals were taken from Nesbet, Noble, and Morgan²⁰ giving a $(2p_\pi, 3p_\pi, 3d_\pi)$ set with exponents 1.084, 1.084, and 2.470, respectively. This basis gave a satisfactory representation of all the states of interest except the $a^3\Sigma_g^+$. This problem was diagnosed as being due to the lack of diffuse σ_g orbitals and the diffuse ($\zeta=0.800$) $2s(\sigma_u)$ orbital was added to the σ_g -orbital set.

This basis was then used to perform full-configuration-interaction (CI) calculations for the six states ($X^1\Sigma_g^+$, $b^3\Sigma_u^+$, $a^3\Sigma_g^+$, $B^1\Sigma_u^+$, $c^3\Pi_u$, $C^1\Pi_u$) of the H_2 target with the H_2 bond length frozen at $R=1.4a_0$. These states constitute the lowest state in each symmetry. Comparison with effectively exact quantum-chemistry calculations²¹ shows that this calculation reproduces all the vertical electronic-excitation thresholds to within 0.4 eV. This relatively minor error was then corrected for by shifting the diagonal elements of our inner-region Hamiltonian matrix.

Scattering calculations were performed using the molecular R -matrix method, details of which can be found elsewhere.²² Because of the diffuse nature of several of the target states, it was necessary to increase the radius of the R -matrix sphere a defining the inner region of the calculation to $20a_0$. This is considerably larger than had previously been used for molecular calculations; as a result it was found necessary to double the number of Gauss-Legendre quadrature points usually used to evaluate the diffuse portion of the integrals.

In the R -matrix method, the target orbitals are augmented in the inner region by sets of continuum functions of appropriate (l, m) generated as the numerical solution of some model problem within a partial-wave ex-

pansion.^{22,23} All solutions with $l \leq 6$ and $m \leq 3$ lying below 5 Ry were included in the final basis. An orthonormal set of molecular orbitals were generated by Lagrange orthogonalizing one orbital from the σ_g , σ_u , and π_g sets to the target and two orbitals from the π_u set.²³ The resulting continuum-orbital set was then Schmidt orthogonalized to the full set of target orbitals.

Inside the R -matrix sphere the (energy-independent) wave function is represented by terms of two types:

$$\Psi_k = \mathcal{A} \sum_i a_{i,k} \Phi_i(x_1, \dots, x_N) F_{i,k}(x_{N+1}) + \sum_j b_{j,k} \phi_j(x_1, \dots, x_N, x_{N+1}), \quad (1)$$

where \mathcal{A} is an antisymmetrization operator. The first term involves a sum over products of target states Φ_i and continuum functions $F_{i,k}$. With a CI target wave function this term is generated by constructing the Hamiltonian matrix elements appropriate for each configuration of the appropriate target representation. These matrix elements are then contracted together using the coefficients of target configurations generated in the relevant target CI calculation. The second term in (1) involves a sum over configurations where all electrons are placed in molecular orbitals belonging to the target. Such terms allow for high- l terms important in the region of the nuclear singularities, relaxation of the orthogonality condition described above, and short-range target-polarization effects. Because we have used a full CI representation of our H_2 target, all possible L^2 terms can be included in our expansion without risk of over-correlating the continuum electron. This will not necessarily be true for calculations using a reduced CI representation of the target.

Having solved the internal-region problem (see Ref. 22), it remains for the energy-dependent solutions to be found in the external region to yield the scattering parameters of the collision system. In the external region the wave function can be expanded as a single-center, no-exchange solution of close-coupling equations with the multipole potential providing the only off-diagonal coupling terms. In this work the diagonal and off-diagonal dipole and quadrupole moments²⁴ were retained in this potential expansion.

We present rules for calculations performed using two ($X^1\Sigma_g^+$, $b^3\Sigma_u^+$), four ($X^1\Sigma_g^+$, $b^3\Sigma_u^+$, $a^3\Sigma_g^+$, $B^1\Sigma_u^+$), and six ($X^1\Sigma_g^+$, $b^3\Sigma_u^+$, $a^3\Sigma_g^+$, $B^1\Sigma_u^+$, $c^3\Pi_u$, $C^1\Pi_u$) target states in the coupled-state expansion. The two-state calculations are similar to those of Baluja, Noble, and Tennyson (BNT),² Schneider and Collins,³ and Lima *et al.*⁴ except for the improved representation of the target and target-polarization effects. Results were obtained for all total symmetries up to and including $^2\Phi_g$, which was found previously² to give converged total cross sections.

Figure 1 compares electronic-excitation cross sections for the $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ process with $^2\Sigma_g^+$ symmetry. The figure gives our results as a function of the number of

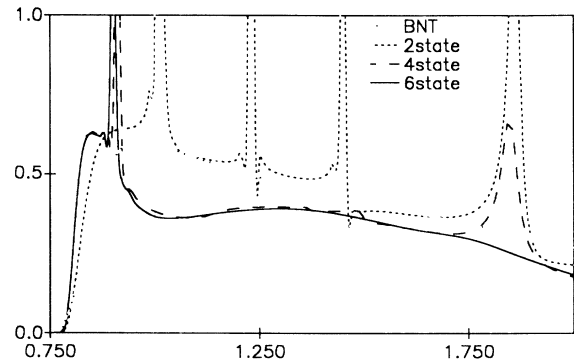


FIG. 1. $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ excitation cross sections, in a_0^2 , as a function of energy, in Ry, for e - H_2 collisions with $^2\Sigma_g^+$ symmetry as a function of the model. The results of Baluja, Noble, and Tennyson (Ref. 2) are shown for comparison.

target states included in the coupled-channel calculation. The results of BNT are also shown for comparison. It is apparent that, neglecting the resonant features introduced in these calculations and discussed below, that our two-state results are in agreement with BNT's. However, our many-state calculations give enhanced cross sections in the near-threshold region and lower cross sections at higher collision energies. We attribute these effects to the improved representation of target polarization and to the loss of flux to other electronic-excitation processes allowed for in these more sophisticated calculations.

A notable feature of Fig. 1 is the resonances introduced in the cross section in the present calculations. Although the high-lying resonances in the two-state calculations are pseudoresonances caused by our neglect of possible open channels in this approximation, the low-lying resonances in the four- and six-state calculations are undoubtedly physical in origin. Several other symmetries showed similar features. We therefore undertook a systematic analysis of the eigenphase sums using an automatic resonance detection and fitting program.²⁵ The results of this search are given in Table I,

TABLE I. Resonance positions E_{res} and widths Γ_{res} for H_2^- with internuclear separation of $1.4a_0$.

Symmetry	E_{res} (eV)	Γ_{res} (eV)	Assignment
$^2\Sigma_g^+$	10.86	1.39	$1\sigma_g^1 1\sigma_u^2$
	12.30	0.073	a
$^2\Sigma_u^+$	10.62		$b^3\Sigma_u^+$ threshold
	10.97		"feature"
	12.76		$c^3\Pi_u$ threshold
$^2\Pi_u$	12.60	0.066	c
$^2\Pi_g$	10.62		$b^3\Sigma_u^+$ threshold
	11.06	0.46	
	11.78	0.96	

where all resonances below the $C^1\Pi_u$ state, the highest included in our calculation, are presented.

Where possible the resonances have been fitted with a Breit-Wigner form. In some cases, notably the $^2\Sigma_u^+$ and $^2\Pi_g$ symmetries, resonancelike features were observed just above the $b^3\Sigma_u^+$ threshold at 10.62 eV. These features, and a similar $^2\Sigma_u^+$ -symmetry one below the $c^3\Pi_u$ threshold, involve jumps in the eigenphase sums too small to be thought of as true resonances. Another feature at 10.97 eV, also of $^2\Sigma_u^+$ symmetry, occurred against a sharply dropping background; it proved impossible to obtain a meaningful fit for its resonance parameters. The other relatively broad resonance in this region, which has $^2\Sigma_g^+$ symmetry, belongs to the well known,^{8,18} repulsive $1\sigma_g^1 1\sigma_u^2$ state of H_2^- .

To make a comparison with the various observed resonance series, labeled *a* to *g*,⁸ it is necessary to allow for the fact we have only considered vertical excitation. If the parent state is known, this can be done by shifting our resonance position by the difference between the vertical excitation energy and the adiabatic excitation energy of the parent.

The *a* and *c* series both have parentage attributed to the $c^3\Pi_u$ state. Allowing for this shifts our second $^2\Sigma_g^+$ and $^2\Pi_u$ resonances to 11.29 and 11.59 eV, respectively. Experimentally these resonances have been assigned to the *a* and *c* series with origins 11.28–11.34 eV and 11.43–11.50 eV.^{8,10} As our widths for these resonances are also consistent with the experimental limits, our results confirm these experimental assignments. Our calculations for the *a* series are in good agreement with nonscattering theoretical estimates.^{16,17} However, the suggestion by Buckley and Bottcher¹⁷ that the *c* series may have $^2\Sigma_u^+$ symmetry is not supported by our results.

Buckley and Bottcher also found a $^2\Sigma_g^+$ series consistent with the *b* series of Comer and Read.¹⁵ We found no such resonance. This series, which was given $B^1\Sigma_u^+$ parentage, has not been observed in several subsequent experimental investigations. It would thus appear that Comer and Read's somewhat tentative interpretation of their observations may not be correct.

The *d* and *e* series have the same energy spacings as the *a* and *c* series, respectively, but different overall symmetry. These series were proposed to explain unusual observed angular distributions. We find no resonances which can be associated with these extra parallel series. Calculated angular distributions for the *a* and *c* resonances suggest that the interpretation placed on the angular distributions of the observed resonances may be too simplistic and that it may not be necessary to cite *d* and *e* series to explain the observations.²⁶

Figure 2 presents total electronic-excitation cross sections for $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$. Our total cross sections have a different shape from those of previous studies which neglected any of the resonance effects discussed above. Unfortunately, the experimental errors, lower limits for

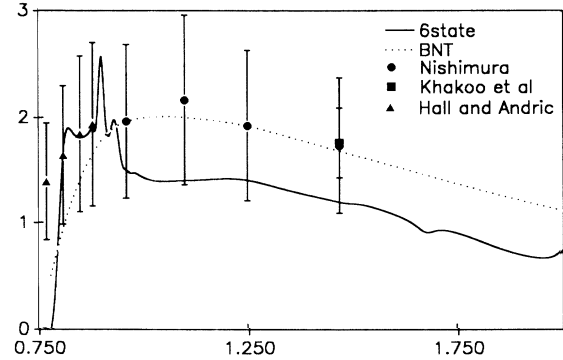


FIG. 2. Total $X^1\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ excitation cross sections, in a_0^2 , as a function of energy, in Ry, for e - H_2 collisions calculated using six coupled states. The results of Baluja, Noble, and Tennyson (Ref. 2) and experiment (Refs. 8, 11, and 13) are shown for comparison.

which are given in the figure, are too large for this structure to be resolved experimentally.

We have also analyzed the electronic-excitation cross sections of the other states in our calculation. Both the $X^1\Sigma_g^+ \rightarrow a^3\Sigma_g^+$ and $X^1\Sigma_g^+ \rightarrow c^3\Pi_u$ cross sections show structure due to the resonances in the near-threshold region. Away from this region the $a^3\Sigma_g^+$ and $c^3\Pi_u$ cross sections are, respectively, about a quarter and a third of that found for the $b^3\Sigma_u^+$ state at the same energy, in line with the limited experimental data on these processes.¹³ Excitation of either of the singlet excited states in our calculation is of similar magnitude. In neither case is there any near-threshold resonance structure.

In this Letter, we have reported full close-coupled electron- H_2 scattering calculations using up to six target states. These states have been accurately represented using specially optimized basis functions and full-configuration interaction. A number of interesting features have been observed in the resulting electronic-excitation cross sections. Analysis of the associated resonances structures lends strong support to the experimental assignment of the *a* and *c* resonance series. Full and differential cross sections for the all electronic-excitation channels will be published elsewhere.²⁶ These calculations will also investigate the effect of including further electronic states, particularly the relatively low-lying $E, F^1\Sigma_g^+$ state, in the coupled-state expansion.

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