Ab Initio Calculations of Vibrationally Resolved Resonances in Electron Collisions with H_2, HD, and D_2

Darian T. Stibbe[1,2] and Jonathan Tennyson[2]
[1]*Institute for Theoretical Atomic and Molecular Physics, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, Massachusetts 02138*
[2]*Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom*

(Received 11 April 1997)

Adiabatic *R*-matrix scattering calculations for vibrationally resolved resonance series *a*, *b*, and *c* are presented and compared with experimental studies for e-H_2, e-D_2, and e-HD. The excellent agreement allows a complete theoretical explanation of the series from which definitive assignments of parentage and symmetry can be made. It also explains the long-standing disagreements among and between previous theoretical and experimental results. More generally, these results provide the first corroboration of the idea of multiple parent states and parent state swapping of Feshbach-type resonances in molecules. [S0031-9007(97)04552-3]

PACS numbers: 34.80.–i

Most molecules have a forest of electronically excited states some 6–12 eV above their electronic ground states. Collisions with electrons at this energy are thus often dominated by multiple resonance series which are difficult to disentangle experimentally or to model theoretically. H_2 is the simplest and most fundamental molecule and the electron-H_2 collision system has been much studied. Even this simplest of systems, however, shows an enormously complicated resonance structure in the 10–15 eV region due to the many electronically excited target states present. The lowest three resonance series, the so-called *a*, *b*, and *c* series have been extensively studied [1] and are the subject of this Letter.

Over the last thirty years, many experiments have studied these resonance series for e-H_2 [2–9] as well as e-D_2 [2,6,7,9,10] and e-HD [7,9]. The standard model for these anionic Feshbach-type resonances is that the electron is temporarily trapped in a potential associated with a particular excited state of the target. This excited target state is usually assigned as the parent of the resonance. However, for H_2^- resonances, there has been much confusion and disagreement over the assignments of parentage and even in the assignment of overall symmetry.

This is the first electron collision calculation of these H_2^- resonances to include nuclear motion although several calculations have been performed at fixed bond length [11–13]. There are an H_2^- quasivariational/stabilization calculation [14] and a variational [15] calculation which have included a treatment of nuclear motion effects. However, as we have shown previously [16], these calculations produce multiple manifestations of the same resonance and their use has led to rather glib analysis and incorrect assignments.

Our recent scattering study [17] suggested that an important feature overlooked in previous experimental and theoretical analysis is that, contrary to the normal assumption, resonances can have multiple parent states and can swap between dominant parents as the bond length is changed. Under these circumstances, the trapping potential is made up of a superposition of interactions with more than one target state. If one parent is dominant, the resonance will appear just below that state. As the bond length changes, the relative importances of the contributions from each parent state can change and different states can dominate. The resonance will thus appear to swap parent state.

Fixed-nuclei (and hence nuclear mass-independent) calculations were performed for H_2 separations, R, of $0.8a_0$ to $4.0a_0$ in steps of $0.1a_0$ using the UK molecular *R*-matrix suite of programs [18]. Target wave functions were represented using a full configuration interaction within a basis set of $4\sigma_g$, $3\sigma_u$, $3\pi_u$, and $3\pi_g$ Slater-type orbitals. These had been energy optimized [19] for the lowest seven target states ($X\ ^1\Sigma_g^+$, $a\ ^3\Sigma_g^+$, $b\ ^3\Sigma_u^+$, $b\ ^1\Sigma_u^+$, $C\ ^1\Pi_u$, $c\ ^3\Pi_u$, $E,F\ ^1\Sigma_g^+$) which were those retained in our close-coupling expansion. It is possible to determine the errors in our target states (≤ 0.1 eV) by comparison with large, and effectively exact, H_2 electronic structure calculations [20–23].

Numerical functions were used to represent the continuum electron in a truncated ($l \leq 6$, $m \leq 3$) partial wave expansion. Calculations are performed for all total symmetries up to $^2\Phi_g$. The resonances considered here are found in the $^2\Sigma_g^+$, $^2\Sigma_u^+$, and $^2\Pi_u$ symmetries. Resonances seen in the $^2\Pi_g$ and the $^2\Delta_g$ symmetries appear to be the series *d* and *e* [1,2] resonances, respectively, but these assignments are more tentative and are not discussed here. Details of the calculation can be found in [16] and [17]; full results will be published elsewhere [19].

When a resonance is detected, it is fitted using the Q-matrix method [16,24] which fits the time delay as a Lorentzian. Use of this method allows resonances to be fitted in situations where other methods can fail [16]. Each resonance was tracked as a function of bond length to give the potential curves of the H_2^- quasibound states. The program LEVEL [25] was used to determine numerically the vibrational state energies of the resonance for each of the three isotopomers. These curves and associated H_2^- vibrational states are presented in Fig. 1. This model ignores the implicitly complex and nonlocal nature of the resonance potential. More sophisticated treatments are available [26] but the longevity of the resonances suggests our simple treatment should be reliable.

To obtain our best *ab initio* estimate, a correction to the resonance positions is made for the error caused by inaccuracies in the parent state energies. Since a resonance can be associated with different, often multiple, parents, at many bond lengths one can only guess at the correction required. Because of this, and since tests showed that including a correction at all bond lengths made little difference to the vibrational spacings, a correction was included only in the absolute position as determined at the lowest point, R_e, of the potential curve of each resonance. Felicitously, for series *a* and *c* which each have two dominant parents at their respective R_e, the parents had the same energy correction. The shifts involved are 0.08 eV for the *a* and *c* series, and -0.08 eV for the *b* series which has one dominant parent at equilibrium.

Series *a* is the best studied of the resonance series and is the only one whose total symmetry, $^2\Sigma_g^+$, has been indisputably determined. Even so, its parentage has been the cause of much debate [16]. There are four target states slightly higher in energy than the resonance ($c\ ^3\Pi_u$, $C\ ^1\Pi_u$, $a\ ^3\Sigma_g^+$ and the inner E region of the $E,F\ ^1\Sigma_g^+$) any of which, from the shape of the resonance potential curve, could be its parent. In a series of two state (ground plus possible parent) calculations we found a resonance associated with each of these states [16] but in multistate calculations, only a single resonance is ever seen. This suggests that the states act in combination as joint parents. The stabilization calculation by Eliezer *et al.* [14] found phantom resonances associated with three of the possible parent states, probably due to a lack of coupling between their target states.

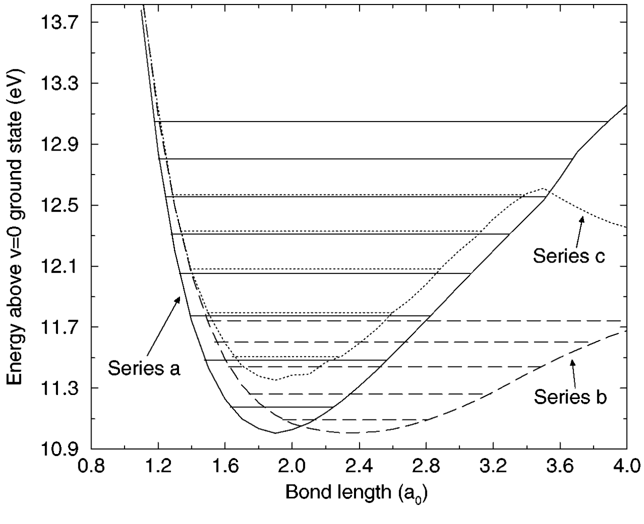

FIG. 1. Uncorrected potential energy curves for the series *a*, *b*, and *c* H_2^- resonances with vibrational positions.

The vibrational energy levels of the series *a* H_2^-, HD^-, and D_2^- states are shown in Table I.

The levels for H_2^- are in superb agreement with all the previous experimental results. For HD^-, the spacings are in good agreement with both comparison experiments although those of Furlong and Newell [9] are around 0.1 eV higher than ours in absolute value. Furlong and Newell's results for the series *c* HD^- resonance (seen in the same run as series *a*) are also around 0.1 eV higher than other experiments which suggests their calibration for HD could be out by this amount. The series *a* results for D_2^- are again in excellent agreement with both measurements, particularly that of Comer and Read [2].

The series *b* resonance is difficult to see experimentally as it decays preferentially to high vibrational levels of the ground state and has been seen only by Comer and Read [2]. They assigned the resonance as $^2\Sigma_g^+$ symmetry due to an apparent angular isotropy. Symmetry assignment through comparison of differential cross sections with an expected form is often unreliable [27] and in this case was based on very little data which could have been contaminated by the isotropic series *a*. This determination is not considered reliable.

In our calculations, a $^2\Sigma_u^+$ resonance in the correct region and with the correct width (≈ 30 meV [2]) is seen and is almost certainly the series *b* resonance. This resonance is found to have multiple parent states of $a\ ^3\Sigma_g^+$ and $b\ ^1\Sigma_u^+$. It follows the $a\ ^3\Sigma_g^+$ state before swapping to the $b\ ^1\Sigma_u^+$ at around $R = 1.7a_0$ [17]. As can be seen from Fig. 1, $R_e^b = 2.33a_0$, much longer than the equilibrium bond length of the ground state. The Franck-Condon overlap between the resonance and the ground state is therefore significant only for high vibrational levels of the ground state which explains why it has been seen only in those channels.

The vibrational levels for series *b* are shown in Table II along with the Comer and Read [2] results.

The interpretation of Comer and Read's experimental results is hampered by several factors. They found that the higher the energy of a resonance vibrational state, the higher the exit channel required to see it. This causes a problem because the energy of the resonance was found to depend on the vibrational exit channel being monitored and it was difficult to extract a "true" resonance energy. Additionally, series *a* vibrational levels in the same region can distort observations of the series *b* positions. It also proved impossible to label definitively the vibrational levels. Comer and Read tried to fit their data to a Morse potential and found that their best fit came about by assuming two missing levels but this fit was poor. Parent swapping by the resonance as the bond length changes explains why a Morse potential is a poor model and so should not be used to find the number of missing levels.

TABLE I. Resonance series a vibrational energy levels relative to ground state $v = 0$.

	H_2^-				HD^-			D_2^-		
Vib. level	This work	Expt. [9]	Expt. [2]	Expt. [28]	This work	Expt. [9]	Expt. [7]	This work	Expt. [2]	Expt. [10]
0	11.30		11.30	11.30	11.28		11.28	11.30	11.32	11.35
1	11.61		11.62	11.62	11.55		11.54	11.52	11.54	11.57
2	11.90	11.92	11.91	11.92	11.82	11.93	11.79	11.73	11.75	11.78
3	12.17	12.21	12.19	12.20	12.05	12.18	12.02	11.94	11.96	11.98
4	12.43	12.48	12.45	12.46	12.28	12.42	12.27	12.14	12.15	12.18
5	12.68		12.68	12.70	12.45		12.49	12.32	12.32	12.36
6	12.93		12.89	12.93	12.72			12.50	12.48	12.54
7	13.17		13.10		12.93			12.68	12.61	12.71

Given all these problems, our results fit remarkably well with those of the experiment assuming there is only one missing level in the experiment. In this case the experiment series b has spacings from $v = 1$ of 0.20, 0.16, 0.12, and 0.10 eV compared with our results of 0.18, 0.16, 0.14, and 0.09 eV. This match allows reassignment of the series b as ${}^2\Sigma_u^+$ symmetry with conviction.

Our calculations show that the series c resonance is ${}^2\Pi_u$ symmetry. This symmetry designation, as well as its parentage, has been the subject of some debate. This is partially fueled by the closeness with which the series c levels follow those of series a (see Fig. 1). Curiously, it appears to have been common practice among experimentalists (for example, [8]) to assign this resonance as ${}^2\Pi_u$ symmetry and then to obtain good agreement with the levels of one of the (phantom) ${}^2\Sigma_g^+$ resonances of Eliezer *et al.* [14].

In our calculation, the ${}^2\Pi_u$ resonance starts off following the $a\ {}^3\Sigma_g^+$ state but then crosses over to follow the $c\ {}^3\Pi_u$ at around $R = 1.7a_0$, where the two thresholds meet. At around $R = 3.5a_0$ it then swaps over to follow the (by now) F outer region of the $E, F\ {}^1\Sigma_g^+$ creating a lip in the potential.

The vibrational energy levels are shown in Table III along with experimental results. The vibrational level labels for Furlong and Newell's [9] D_2 experiment have been reassigned to fit with other experiments. The results given in brackets are energy levels close to the lip of the potential curve and are computed as if the curve continues without swapping to the $E, F\ {}^1\Sigma_g^+$ state. Without more points on the potential curve in the swapover area, it is impossible to compute reliably the levels in this region.

TABLE II. Resonance series b vibrational energy levels relative to the ground state $v = 0$.

	H_2^-		HD^-	D_2^-
Vib. level	This work	Expt. [2]	This work	This work
0	11.05		11.08	11.10
1	11.22		11.23	11.22
2	11.40	11.27	11.38	11.35
3	11.56	11.47	11.52	11.47
4	11.70	11.63	11.66	11.70
5	11.79	11.75	11.83	11.79
6		11.85		

The vibrational labeling used in Table III for the energy levels of series c is determined by the existence of the 11.19 eV level from [3] in H_2^- and the 11.25 eV level from [10] in D_2^-. Under the assumption that these are correct, our results appear to be just over 0.4 eV above the experimental results for all the isotopomers, with excellent matching between the vibrational spacings, particularly for the lower levels. If on the other hand those two levels are not correct or are actually due to another resonance, then all the experimental results would be shifted down by one level and our results would then be too high by around 0.14 eV for the H_2^-, either 0.08 or 0.20 eV too high for the HD^-, and 0.21 eV too high for the D_2^-.

It is interesting to note how the spacings of the highest vibrational levels in [9] for D_2 suddenly drop between $v = 6$ and $v = 9$. This would be expected if the potential curve were to level out at higher energy, exactly as is seen in our results, where the resonance swaps to the $F\ {}^1\Sigma_g^+$ state.

The overestimate of the absolute energy positions of the series c comes about for two reasons. First, for this series the fixed-nuclei resonance positions are difficult for us to pinpoint accurately [19] due to the proliferation of target thresholds. This is particularly true near $R_e^c \approx 1.9a_0$, where three target thresholds (including the two dominant parents of the resonance) intersect. The difficulty in finding the resonance positions yields a potential curve which is not smooth in this region. The result is an uncertainty in the absolute positions of the vibrational series of around 0.05 eV. The low-lying vibrational level spacings will also be affected to different extents for the different isotopomers.

The second source of error affects only non-Σ symmetries for which the representation of polarization effects is poorer. Our calculation uses only σ and π orbitals as target basis functions. When calculating polarization effects in the case of ${}^2\Pi_u$ symmetry, the absence of δ_g functions in the basis or ${}^2\Delta_g$ states in our close-coupling expansion results in an underestimate of the effect. It is thus expected for the results for series c to be too high. No correction is attempted for this.

TABLE III. Resonance series *c* vibrational energy levels relative to the ground state $v = 0$.

	H_2^-				HD^-			D_2^-			
Vib. level	This work	Expt. [9]	Expt. [3]	Expt. [28]	This work	Expt. [9]	Expt. [7]	This work	Expt. [9]	Expt. [2]	Expt. [10]
0	11.63		11.19		11.64			11.67			11.25
1	11.92		11.50	11.50	11.89		11.47	11.87			11.45
2	12.20	11.78	11.80	11.79	12.14	11.82	11.70	12.07		11.65	11.67
3	12.45	12.07	12.07	12.08	12.37	12.07	11.95	12.27	11.88	11.87	11.89
4	(12.69)	12.34		12.38	(12.58)	12.32	12.19	12.45	12.07	12.07	12.09
5		12.59			(12.77)	12.55	12.42	(12.63)	12.27	12.23	12.28
6		12.84				12.78	12.65	(12.79)	12.47		12.47
7									12.62		12.64
8									12.77		
9									12.84		

In conclusion, the vibrational level energy positions have been found for the series *a*, *b*, and *c* resonances in *e*-H_2, *e*-D_2, and *e*-HD collisions for the first time. The values for the resonance series *a* fit perfectly with experiment for all the isotopomers both in absolute energy and in vibrational spacing. The vibrational spacings for series *b* agree well with the only experimental observation of the series which we reclassify as $^2\Sigma_u^+$ symmetry. Similarly for series *c*, the vibrational spacings are very close to those of the experiments although the absolute position is too high by about 0.4 eV (or possibly 0.2 eV with a relabeling of vibrational levels) probably due to poor representation of polarization effects for this symmetry. The results give, for the first time, a complete, definitive set of symmetry labels for these resonance series clearing up many years of confusion and disagreement.

All three H_2^- series studied were found to have multiple parent states. Series *b* and *c* swapped parents as a function of bond length, contrary to previous models which always associated a resonance with a single parent. The excellent agreement with experiment for the vibrational levels provides a useful corroboration of these phenomena which could prove to be important in other areas where resonances are prominent.

The authors thank Nigel Mason for useful discussions and the U.K. Engineering and Physical Science Research Council for financial support. This work was also supported by the U.S. National Science Foundation through a grant for ITAMP at Harvard University and the Smithsonian Astrophysical Observatory.

[1] G. J. Schultz, Rev. Mod. Phys. **45**, 423 (1973).
[2] J. Comer and F. H. Read, J. Phys. B **4**, 368 (1971).
[3] G. Joyez, J. Comer, and F. H. Read, J. Phys. B **6**, 2427 (1973).
[4] A. Weingartshofer, H. Ehrhardt, V. Hermann, and F. Linder, Phys. Rev. A **2**, 294 (1970).
[5] S. B. Elston, S. A. Lawton, and F. M. Pichanick, Phys. Rev. A **10**, 225 (1974).
[6] L. Sanche and G. J. Schultz, Phys. Rev. A **6**, 69 (1972).
[7] C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, J. Chem. Phys. **44**, 437 (1966).
[8] N. J. Mason and W. R. Newell, J. Phys. B **19**, L203 (1986).
[9] J. M. Furlong and W. R. Newell, J. Phys. B **28**, 1851 (1995).
[10] A. Weingartshofer and M. Eyb, J. Phys. B **8**, L278 (1975).
[11] S. E. Branchett, J. Tennyson, and L. A. Morgan, J. Phys. B **23**, 4625 (1990).
[12] S. E. Branchett and J. Tennyson, Phys. Rev. Lett. **64**, 2889 (1990).
[13] A. J. R. da Silva, M. A. P. Lima, L. M. Brescansin, and V. McKoy, J. Chem. Phys. **41**, 2903 (1990).
[14] I. Eliezer, H. S. Taylor, and J. K. J. Williams, J. Chem. Phys. **47**, 2165 (1967).
[15] B. D. Buckley and C. Bottcher, J. Phys. B **10**, L636 (1977).
[16] D. T. Stibbe and J. Tennyson, J. Phys. B **29**, 4267 (1996).
[17] D. T. Stibbe and J. Tennyson, J. Phys. B **30**, L301 (1997).
[18] C. J. Gillan, J. Tennyson, and P. G. Burke, in *Computational Methods for Electron Molecule Collisions*, edited by W. M. Huo and F. Gianturco (Plenum Press, New York, 1995), pp. 239–252.
[19] D. T. Stibbe and J. Tennyson (to be published).
[20] W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965).
[21] L. Wolniewicz and K. Dressler, J. Chem. Phys. **82**, 3292 (1985).
[22] L. Wolniewicz and K. Dressler, J. Chem. Phys. **82**, 3861 (1988).
[23] W. Kolos and J. Rychlewski, J. Mol. Spectrosc. **169**, 341 (1995).
[24] F. Smith, Phys. Rev. **114**, 349 (1960).
[25] R. J. Leroy, University of Waterloo Chemical Physics Research Report No. CP-55R, 1996.
[26] W. Domcke, Phys. Rep. **208**, 97 (1991).
[27] N. J. Mason (private communication).
[28] A. Weingartshofer, E. M. Clarke, J. K. Holmes, and J. W. McGowan, J. Phys. B **8**, 1552 (1975).