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# Millimetre-wave Electronic Spectrum of the $D_2^+$ Ion

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We have extended our earlier microwave and IR measurements of the $2p\sigma_u$–$1s\sigma_g$ electronic spectrum of $D_2^+$ into the millimetre-wave region of the spectrum, and report the measurement of a further eight vibration–rotation components. The measured transition frequencies and the nuclear hyperfine splittings are very close to those predicted by the best *ab initio* calculations.



In earlier papers we have described the microwave electronic spectra of $H_2^+$[1–4] and $D_2^+$[4,5] involving vibration–rotation levels of the ground and first excited electronic states which lie close to the dissociation limit. The $1s\sigma_g$ ground-state potential has an adiabatic dissociation energy $D_e$ of 22 529 $cm^{-1}$, supporting 20 vibrational levels in $H_2^+$ and 28 in $D_2^+$. The $2p\sigma_u$ excited-state potential is repulsive at internuclear distances, $r$, less than 10.6 $a_0$, but possesses a shallow minimum of 13.3 $cm^{-1}$ depth at $r = 12.47$ $a_0$, arising from the charge–induced-dipole interaction. This potential supports one vibrational level for $H_2^+$ and two for $D_2^+$. Electronic transitions between the highest levels of the ground state and the levels of the long-range state occur in the microwave and millimetre-wave regions of the spectrum. We have previously reported four such transitions for $H_2^+$ and seven for $D_2^+$. With the acquisition of higher-frequency millimetre-wave sources we have now been able to observe a further eight transitions in $D_2^+$, the details of which are described in this paper.

Fig. 1 shows the Born–Oppenheimer potential curves for the two relevant electronic states in the region near the lowest dissociation limit. We also show the positions of the $v = 26$ and 27 vibration–rotation levels of the ground state, and the $v = 0$ and 1 levels of the excited state. The details of our experimental methods have been described elsewhere[2,5] and will be discussed only briefly here. The ions are formed by electron impact ionisation of the neutral precursor molecules, and because of relatively favourable Franck–Condon factors, the highest levels of the ground electronic state are populated. The ions are accelerated to potentials of several kV, and the resulting beam is mass-analysed with a magnetic sector. After passing through a rectangular waveguide section of length 40 cm, the ion beam enters an electric field lens, where fields up to 40 kV $cm^{-1}$ may be applied. Energy levels lying within *ca.* 5 $cm^{-1}$ of the dissociation limit undergo fragmentation in the lens, producing atomic ion fragments with characteristic kinetic energies, which are energy-analysed by means of an electrostatic sector and detected with an off-axis electron multiplier. The fragmentation process may be made state-selective by suitable choice of the electric field strength and electrostatic analyser voltage. Microwave or millimetre-wave transitions induced in the waveguide result in population transfer between energy levels and consequent changes in fragment ion intensity, which are detected. The microwave radiation is amplitude-modulated at 6.7 kHz, so that ac detection techniques can be used to observe the microwave resonances.

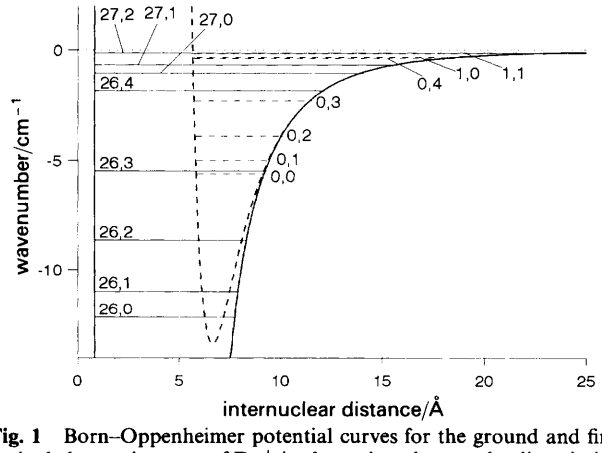


**Fig. 1** Born–Oppenheimer potential curves for the ground and first excited electronic states of $D_2^+$ in the region close to the dissociation limit. The positions of the vibration–rotation levels of the long-range $2p\sigma_u$ state are shown by dashed lines, and the $v = 26$ and 27 vibration–rotation levels ($v$, $N$) of the $1s\sigma_g$ ground state are shown by continuous lines.

The resonance lines described in this paper span the frequency range 110 to 215 GHz. Our primary radiation source is a 0 to 40 GHz synthesiser, which is frequency-multiplied by means of Millitech active sextuplers to produce radiation (1 mW power) over the range 110 to 170 GHz. We have, however, observed that there is also sufficient eight-fold frequency multiplication to allow us to extend our observations to 215 GHz. We have used a WR-28 waveguide, with a rectangular cross-section of 7.11 mm × 3.56 mm, for the transition region. As we have described elsewhere,[6] at frequencies above 40 GHz the radiation propagates in more than one mode; each mode has a characteristic phase velocity giving rise to an associated Doppler-shifted resonance line. Fig. 2 (top) shows the resonance with a rest frequency of 152 896.5 MHz, with the modes identified. These all correspond to Doppler shifts arising from parallel propagation of the ion beam and microwave radiation; a corresponding set of antiparallel mode resonances is also observed so that in this case extrapolation to zero ion-beam velocity to obtain the rest frequency is straightforward and accurate. In the cases of the highest frequency resonances, however, the millimetre-wave power level was too low to observe the full mode pattern. Rest frequencies were therefore obtained by following the frequency shift of a particular (unidentified) mode at different ion beam potentials. Our linewidths are determined by the transit time of the ions through the waveguide region, and are typically 600 to 700 kHz.

The full results for $D_2^+$, including our earlier measurements, are presented in Table 1, together with the transition assignments. These are based on extremely accurate *ab initio* calculations carried out by Moss[7] which have been described elsewhere. The theoretical frequencies are also given in Table 1, and are seen to agree with the experimental values to within a few MHz (*i.e. ca.* 0.0001 $cm^{-1}$). We have also made some further observations of the nuclear hyperfine splitting, which we have discussed previously.[3,5] The total nuclear spin, $I$, for $D_2^+$ takes the values 2, 1 or 0; the nuclear and electron spins are strongly coupled to each other, but weakly

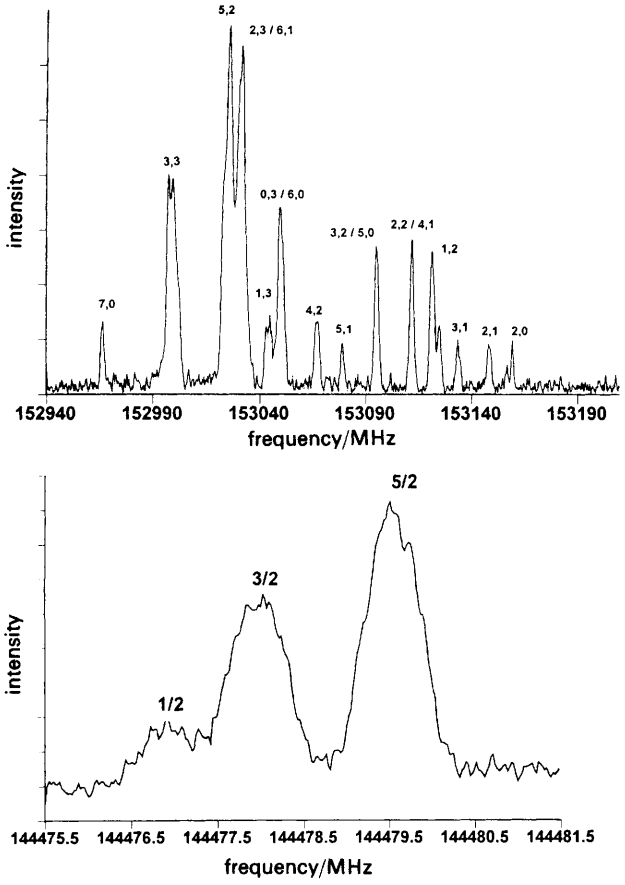


**Fig. 2** (top) Parallel Doppler-shifted mode pattern for the $D_2^+$ transition with a rest frequency of 152 896.5 MHz. The $m$, $n$ values for the (degenerate) $TE_{m,n}$ and $TM_{m,n}$ modes are shown; (bottom) Deuteron hyperfine structure for the transition with a rest frequency of 144 299.0 MHz. The $G$ values are shown on the spectrum.

coupled to the molecular rotation, $N$. We can describe the hyperfine states by specifying the allowed values of $G$ which result from the coupling $G = S + I$. Ground-state rotational levels of even $N$ have a total deuteron nuclear spin $I$ of 0 or 2 (so that $G$ may take values 1/2, 3/2 or 5/2), whereas the excited-state levels are associated with $I = 1$ (with $G = 1/2$ or 3/2 only). The Fermi contact interaction between $S$ and $I$ is expected to be large (close to one half of the free atom value of 218.5 MHz for each deuteron), but adiabatic calculations indicate that this interaction will also be closely similar in magnitude for both the ground and excited-state levels involved in our experiments. Since the electron spin–rotation interaction is extremely small, all of the electric-dipole transitions described in this paper are necessarily diagonal in the quantum number $G$. Consequently, resolved hyperfine splitting is not expected, and it was with some considerable surprise that we earlier observed splitting in the spectra of both $H_2^+$ and $D_2^+$. We now understand the origin of this splitting, which has been termed 'nuclear hyperfine symmetry breaking'. The u and g symmetry labels which are conventionally used to differentiate between the two electronic states are only approximate labels because the inversion operation, $i$, does not commute with those parts of the molecular Hamiltonian involving nuclear spin. The operation $p_{12}$, which interchanges the nuclear spins, is also only a near-symmetry operation, but the combination $ip_{12}$ is a true symmetry operation of the total Hamiltonian, showing that certain hyperfine levels of the ground and excited electronic states may be coupled by the Fermi contact interaction. Moss has calculated[8] the magnitudes of the coupling for high-lying levels in both $H_2^+$ and $D_2^+$, and we have shown that there is excellent agreement between the theoretical and experimentally measured splittings. This good agreement continues to be observed for the $D_2^+$ transitions described in this paper, as the results in Table 1 demonstrate. An example of hyperfine structure is shown in Fig. 2 (bottom).

It is possible to carry out a conventional anharmonic oscillator analysis for the long-range charge–induced-dipole state of $D_2^+$, using our measured transition frequencies. This procedure must be regarded as approximate, because of the small number of bound vibration–rotation levels, and also because of the extreme anharmonicity. Nevertheless, we can derive rotational constants for the $v = 0$ level, obtaining the values (and standard deviations) $B_0 = 8554(43)$ MHz,; $D_0 = 41(2)$ MHz.

**Table 1** Comparison of experimental and theoretical transition frequencies and hyperfine splittings

| upper state | lower state | experimental frequency /MHz | predicted frequency[a] /MHz | experimental hyperfine splittings[b]/MHz | predicted hyperfine splittings[b,c]/MHz |
|---|---|---|---|---|---|
| $2p\sigma_u$ 1, 0 | $1s\sigma_g$ 27, 1 | 11 138.1 (4) | 11 145 | unresolved | +0.5 (3/2–1/2) |
| $1s\sigma_g$ 26, 4 | $2p\sigma_u$ 0, 3 | 11 928.0 (3) | 11 927 | unresolved | −0.4 (5/2–3/2) |
| | | | | | −0.2 (3/2–1/2) |
| $2p\sigma_u$ 1, 1 | $1s\sigma_g$ 27, 0 | 25 755.4 (4) | 25 759 | unresolved | +0.6 (5/2–3/2) |
| | | | | | +0.3 (3/2–1/2) |
| $2p\sigma_u$ 0, 2 | $1s\sigma_g$ 26, 3 | 48 064.3 (4) | 48 064 | unresolved | <0.2 |
| $1s\sigma_g$ 27, 2 | $2p\sigma_u$ 0, 3 | 64 290.9 (1)[d] | 64 290 | −1.66 (5/2–3/2) | −1.63 (5/2–3/2) |
| | | | | −1.14 (3/2–1/2) | −1.08 (3/2–1/2) |
| $1s\sigma_g$ 27, 1 | $2p\sigma_u$ 0, 2 | 95 222.5 (1) | 95 221 | unresolved | −0.4 (3/2–1/2) |
| $2p\sigma_u$ 0, 1 | $1s\sigma_g$ 26, 2 | 109 672.8 (1) | 109 675 | unresolved | <0.2 |
| $1s\sigma_g$ 27, 0 | $2p\sigma_u$ 0, 1 | 118 296.7 (4) | 118 296 | unresolved | −0.5 (5/2–3/2) |
| | | | | | −0.3 (3/2–1/2) |
| $1s\sigma_g$ 27, 2 | $2p\sigma_u$ 0, 1 | 144 299.0 (6)[d] | 144 299 | −1.58 (5/2–3/2) | −1.57 (5/2–3/2) |
| | | | | −1.08 (3/2–1/2) | −1.05 (3/2–1/2) |
| $1s\sigma_g$ 27, 1 | $2p\sigma_u$ 0, 0 | 144 895.2 (4) | 144 895 | unresolved | −0.4 (3/2–1/2) |
| $2p\sigma_u$ 0, 4 | $1s\sigma_g$ 26, 3 | 152 896.5 (5) | 152 899 | unresolved | +0.2 (3/2–1/2) |
| $2p\sigma_u$ 0, 0 | $1s\sigma_g$ 26, 1 | 162 165.2 (6) | 162 169 | unresolved | <0.1 |
| $2p\sigma_u$ 0, 3 | $1s\sigma_g$ 26, 2 | 189 681 (5) | 189 684 | unresolved | +0.2 (5/2–3/2) |
| | | | | | +0.1 (3/2–1/2) |
| $2p\sigma_u$ 0, 2 | $1s\sigma_g$ 26, 1 | 211 847 (5) | 211 842 | unresolved | <0.1 |
| $2p\sigma_u$ 0, 1 | $1s\sigma_g$ 26, 0 | 215 484 (5) | 215 479 | unresolved | <0.2 |

The figures in parentheses indicate the error in the last figure quoted. [a] Ref. 7. [b] Sign of splitting derived relative to the $G = 5/2$ component (whether present or not). [c] Ref. 8. [d] Rest frequency measured using the $G = 5/2$ component.

The observations described in this paper, and those published earlier, show that both the ground- and excited-state levels are populated in our ion beam. Significant population of high-lying vibration–rotation levels of the ground state is understandable in terms of the direct electron impact ionisation process. Using Born–Oppenheimer potential functions for the $D_2$ and $D_2^+$ ground electronic states, we have calculated the Franck–Condon factors for ionisation using the program LEVEL, described by Le Roy.[9] Our results, which are in good agreement with those published by other workers,[10] show that even the ground-state vibration–rotation levels lying close to the dissociation limit have significant population factors, of the order of $10^{-4}$, which are high enough to permit our spectroscopic observations. However, similar calculations involving the $D_2^+$ excited $2p\sigma_u$ electronic state, which has its potential minimum at a much larger internuclear distance, result in negligible population ($<10^{-14}$) of its vibration–rotation levels. We must conclude, therefore, that the observed population of these levels arises from secondary processes in the ion source, perhaps involving ion–molecule collisions.

The results described in this paper, together with those reported earlier, show that for the one-electron molecules $H_2^+$ and $D_2^+$, the agreement between experiment and the best theory is extraordinarily good; the worst discrepancies are only a few MHz (*ca.* 0.0001 $cm^{-1}$). In order to achieve this level of agreement, the theory must deal adequately with non-adiabatic, relativistic and radiative effects.

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