Observation of the $2p\sigma_u$-$1s\sigma_g$ Electronic Spectrum of D_2^+

Alan Carrington, Iain R. McNab, and Christine A. Montgomerie
Department of Chemistry, University of Southampton, Hampshire SO9 5NH, England
(Received 20 July 1988)

The long-range van der Waals state of D_2^+ has been characterized through observations of electronic transitions from the ground state.

PACS numbers: 33.10.Jz, 33.20.Ea, 34.20.Cf

We report the first observation of an electronic spectrum of D_2^+, arising from transitions between high-lying vibration-rotation levels of the $1s\sigma_g$ ground state and the vibration-rotation levels of the long-range van der Waals $2p\sigma_u$ state. The interaction of a hydrogen atom with a proton constitutes the simplest interatomic system. At large internuclear distances (R) the important interaction[1] is the attractive charge-induced-dipole term (R^{-4}). As the internuclear distance decreases the valence forces become dominant, being attractive for the $1s\sigma_g$ ground state and repulsive for the $2p\sigma_u$ excited state. The resulting potential-energy curves are illustrated in Fig. 1, which also shows the positions of the relevant D_2^+ vibration-rotation levels studied in this work.

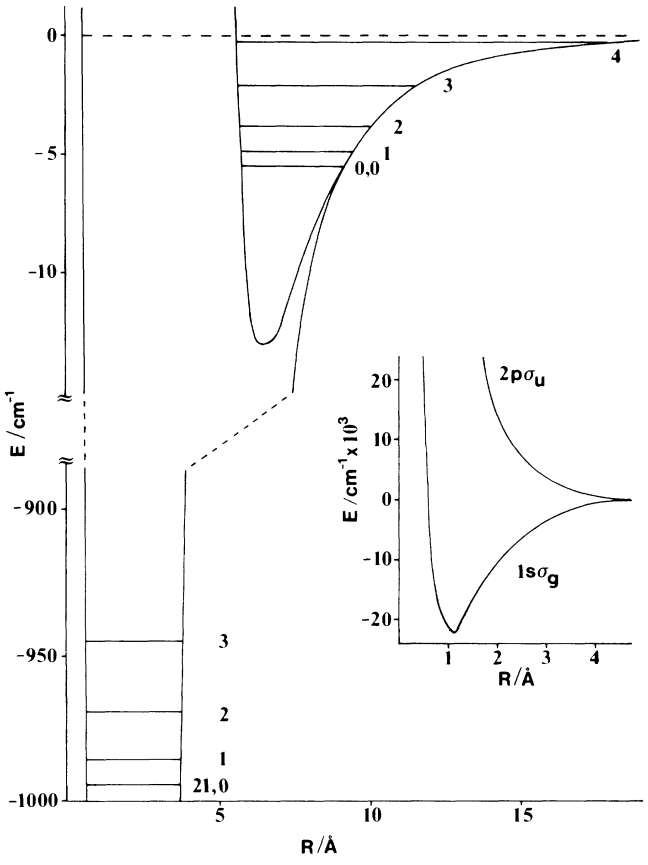

FIG. 1. Sections of the adiabatic potential curves for D_2^+ in the ground $1s\sigma_g$ and excited van der Waals $2p\sigma_u$ states. The positions of the vibration-rotation levels studied are shown.

The apparatus used has recently been described.[2,3] D_2^+ ions are produced by electron impact ionization of D_2 and are accelerated to potentials of up to 5 kV. After initial mass analysis the D_2^+ ion beam is focused into a drift tube where it is brought into collinear coincidence with an appropriate line from a continuous-wave carbon dioxide infrared laser. Doppler tuning and modulation voltages are applied to the drift tube. The ion beam then passes through an electric field of up to 10^4 V cm^{-1} where selective dissociation of weakly bound ions occurs.[4-6] The resulting D^+ fragments are focused into a small magnetic sector and detected with an electron multiplier; the fragment ion current is processed with a lock-in amplifier referenced at the Doppler modulation frequency.

The electron impact ionization of D_2 produces D_2^+ ions with significant populations of all the vibrational levels of the ground state, and it was apparent to us that transitions from $v=21$ to the long-range $2p\sigma_u$ state would lie in the infrared region spanned by the carbon dioxide laser. Although the $2p\sigma_u$-$1s\sigma_g$ electronic transition moment is large, the potential curves shown in Fig. 1 suggest that the Franck-Condon factors will be extremely small. They will, however, be largest for high vibrational levels of the ground state, and laser powers of up to 40 W are available to drive the desired transitions.

The magnetic sector acts as a momentum analyzer and separates the D^+ fragments formed in the field dissociation lens from all other D^+ fragment ions. We have recently demonstrated[3] the extremely high sensitivity provided by this technique in the study of the vibration-rotation spectrum of Hd^+, and it has proved to be equally effective in the present work. We have detected and measured seven transitions, involving all of the bound levels of the van der Waals state predicted by theory (see below). Two examples of the transitions observed are shown in Fig. 2, where we note that at high laser powers signal-to-noise ratios of up to 500 to 1 can be obtained with a 1-s output time constant. The most difficult transitions to observe are those involving the levels with the lowest dissociation energies; electric field dissociation

© 1988 The American Physical Society

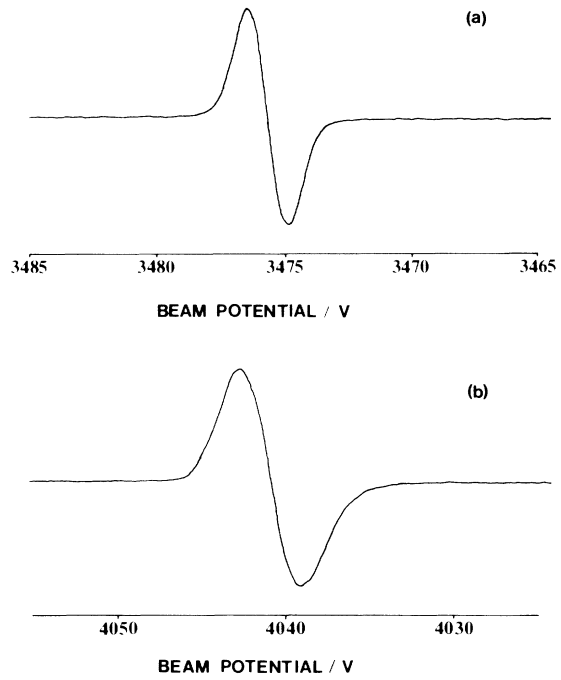

FIG. 2. Examples of observed transitions. (a) $2p\sigma_u(0,0)$-$1s\sigma_g(21,1)$ observed using 20-W laser power on $^{12}CO_2$ $R(30)$ 00°1-10°0 aligned in parallel coincidence with the ion beam. (b) $2p\sigma_u(0,1)$-$1s\sigma_g(21,2)$ observed using 20-W laser power on $^{12}CO_2$ $R(6)$ 00°1-10°0 aligned in parallel coincidence with the ion beam.

occurs so readily it is difficult to separate cleanly the desired fragment D^+ ions from the background. The transitions are still observable at a laser power of 1 W, and the observed linewidths (typically 10 to 20 MHz) are only slightly smaller than those found at high powers. We are unable to resolve any hyperfine structure although some evidence of further splitting is apparent from the shapes of the low power lines.

Our assignment of the observed lines is based upon a modification of adiabatic calculations of the vibration-rotation levels of Hunter, Yau, and Pritchard[7] for the ground state, and adiabatic vibration-rotation levels of Kennedy[8] for the upper state. Nonadiabatic calculations for H_2^+ and HD^+ have been described by Wolniewicz and Poll.[9] Multiplying their nonadiabatic corrections by the reduced masses, and plotting the results against dissociation energy provides nonadiabatic corrections for D_2^+ (-0.525 cm^{-1} for $v=21$). We have no means of assessing the nonadiabatic corrections for the $2p\sigma_u$ state, but they are likely to be small. Table I lists our experimental results and the theoretical transition wave numbers and dissociation energies from the approximate nonadiabatic calculations, and the agreement is seen to be very satisfactory. Of the nine possible rotational components of the 1-21 band we have observed five; two of the possible three components of the 1-21 band have been measured. Analysis of the results provides the following values of the rotational constants (with sign conventions according to Herzberg[10]) and bond lengths for the $2p\sigma_u$ van der Waals state:

$$B_0=0.2864\ \text{cm}^{-1},\ D_0=0.0014\ \text{cm}^{-1},\ R_0=7.7\ \text{Å},$$

$$B_1=0.081\ \text{cm}^{-1},\ R_1=14.4\ \text{Å},$$

$$B_e=0.3891\ \text{cm}^{-1},\ \alpha_e=0.2054\ \text{cm}^{-1},\ R_e=6.6\ \text{Å}.$$

TABLE I. Theoretical dissociation energies, transition wave numbers, and experimental results (all in cm^{-1}).

$2p\sigma_u$ state		$1s\sigma_g$ state				
v,N	Energy	v,N	Energy	Experiment	Theory	Diff.
0,0	−5.513	21,1	−986.285	980.760	980.772	−0.012
0,1	−4.953	21,2	−969.805	964.833	964.852	−0.019
0,2	−3.856	21,3	−945.275	941.398	941.419	−0.021
0,3	−2.283	21,2	−969.805	967.500	967.522	−0.022
0,4	−0.359	21,3	−945.275	944.896	944.916	−0.020
1,0	−0.308	21,1	−986.285	985.963	985.977	−0.014
1,1	−0.147	21,2	−969.805	969.640	969.658	−0.018

Our determination of the rotational constant B_1 requires, at present, the inclusion of the theoretical value for the 21,1-21,2 separation. Five possible transitions remain to be detected, and their measurement will improve slightly the accuracy of our determination of the rotational constants. The van der Waals well depth is predicted by adiabatic calculations to be 13.345 cm^{-1}.

The spin-rotation and deuterium dipolar hyperfine constants are likely to be very small, but the Fermi contact hyperfine interactions are expected to be close to 109 MHz (that is, half of the free-atom value). However, any observed hyperfine splitting of the vibration-rotation lines can arise only from differences in hyperfine constants between the lower and upper states; these differences are clearly very small. It is particularly significant that even the 1,1-21,2 transition shows no splitting. Although the 1,1 level of the $2p\sigma_u$ state lies only 0.147 cm^{-1} below the $D+D^+$ dissociation limit, our results show that the inversion symmetry of the electronic state is preserved. This is in marked contrast with our observations for the HD^+ ion[2,3] where extreme asymmetry in the electron distribution is found for levels close to the $D+H^+$ dissociation limit.

The $2p\sigma_u$-$1s\sigma_g$ spectrum of H_2^+ unfortunately falls outside the region covered by the carbon dioxide laser, although studies with a carbon monoxide laser might be possible. The analogous HD^+ spectrum is accessible, but the van der Waals levels lie above the $H^+ + D$ dissociation limit and may predissociate too rapidly[11] to be observable by spectroscopic methods. Further discussion of these matters, and a full description of the apparatus and results, will be presented in due course.

Our initial attempts to observe the spectrum described

in this paper were based upon monitoring the infrared photodissociation of the $2p\sigma_u$ state, and we are indebted to Dr. N. Bjerre of Aarhus University for drawing our attention to the electric field dissociation of ions. We are grateful to Dr. R. A. Kennedy for supplying us with the results of his adiabatic calculations. One of us (A.C.) thanks the Royal Society for a Research Professorship, another (I.R.M.) thanks the Univeristy of Southampton for a Research Fellowship, and another (C.A.M.) thanks the British Petroleum Company plc. for a Research Studentship. We are indebted to the Science and Engineering Research Council (U.K.) for research grants towards the purchase of equipment.

[1]C. A. Coulson, Proc. Roy. Soc. Edinburgh, Sect. A **61**, 20 (1941); C. A. Coulson and C. M. Gillam, Proc. Roy. Soc. Edinburgh, Sect. A **62**, 360 (1948); M. K. Krogdahl, Astrophys. J. **100**, 311 (1944); J. M. Peek, J. Chem. Phys. **50**, 4595 (1969).

[2]A. Carrington, I. R. McNab, and C. A. Montgomerie, Mol. Phys. **64**, 679 (1988).

[3]A. Carrington, I. R. McNab, and C. A. Montgomerie, Chem. Phys. Lett. (to be published).

[4]J. R. Hiskes, Phys. Rev. **122**, 1207 (1961).

[5]A. C. Riviere and D. R. Sweetman, Phys. Rev. Lett. **5**, 560 (1960).

[6]N. Bjerre and S. R. Keiding, Phys. Rev. Lett. **56**, 1459 (1986).

[7]G. Hunter, A. W. Yau, and H. O. Pritchard, At. Data Nucl. Data Tables **14**, 11 (1974).

[8]R. A. Kennedy, unpublished.

[9]L. Wolniewicz and J. D. Poll, Mol. Phys. **59**, 953 (1986).

[10]G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950), p. 103.

[11]J. P. Davis and W. R. Thorson, Can. J. Phys. **56**, 996 (1978).