FIRST-ORDER STARK EFFECT AND ELECTRIC DIPOLE MOMENT OF H₃P...HC¹⁵N BY PULSED-NOZZLE FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY

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The first-order Stark effect in the $J = 4 \leftarrow 3$, K = 1 transition of the weakly bound dimer H₃P...HC¹⁵N has been observed and measured by pulsed-nozzle Fourier-transform microwave spectroscopy under the selection rules $\Delta M = 0$ and $\Delta M = \pm 1$. The electric dipole moment $\mu = 4.046(47)$ D determined for H₃P...HC¹⁵N has been interpreted in terms of an enhancement $\Delta \mu = 0.60$ D on dimer formation.

1. Introduction

Pulsed-nozzle Fourier-transform microwave spectroscopy is proving a fruitful method for investigating the ground-state rotational spectra of weakly bound molecular dimers [1]. Analysis of the spectra so observed allows the accurate determination of rotational constants, centrifugal distortion constants and various hyperfine coupling constants (especially nuclear quadrupole and nuclear spin-nuclear spin coupling constants). By the use of suitable models, the spectroscopic constants can then be interpreted to give properties of the dimer (e.g. geometry, dynamics of the subunits within the dimer, and electric charge rearrangement on complex formation). Another molecular property of interest is the electric dipole moment of the dimer and this can be determined from the rotational Stark effect.

We have recently modified the pulsed-nozzle, FT microwave spectrometer built at University College London so that we can observe and measure the rotational Stark effect in weakly bound dimers. We report here the first-order Stark effect in the $J = 4 \leftarrow 3$, K = 1ground-state transition of the symmetric-top molecule $H_3P...HC^{15}N$ and from it determine the electric dipole moment $\mu = 4.046(47)$ D. We interpret this value of μ in terms of an enhancement of 0.60 D over the vector sum of the electric dipole moments of the components.

2. Experimental

The spectrometer at University College London is of the Balle-Flygare type [2] and has been briefly described [3]. In order to apply a static uniform electric field to the molecules in the supersonically expanded gas pulse when they are between the Fabry-Pérot mirrors, we have inserted a pair of parallel plates symmetrically between the mirrors, with the nozzle-diffusion pump axis forming one symmetry axis and the line between the centre of the mirrors the other. The 26 cm square plates were constructed from 3 mm thick, flat steel plate. In these experiments, a nominal spacing of 20.0 cm was maintained between the plates by slotting them into accurately machined grooves in a teflon framework which was attached to the mirror-support rods. By placing the plates in other grooves, other separations are possible. We applied a potential of $\frac{1}{2}V$ to one plate and $-\frac{1}{2}V$ to the other while the stainless steel vacuum chamber was maintained at earth potential. A homogeneous electric field of strength $\epsilon = V/d$ was created at the centre of the plates, near to the axis of the Fabry-Pérot mirrors. Potential differences used were in the range 0-100 V and were measured with an accuracy of ± 10 mV with a $4\frac{1}{2}$ digit voltmeter

In the conventional configuration of the input/output waveguide coupling to the Fabry—Pérot mirrors (broad face of the waveguide horizontal), the above

0 009-2614/84/S 03.00 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) arrangement of the parallel plates ensures that the electric vectors of the microwave radiation and the applied static field are perpendicular. The selection rules for transitions when the field strength $\epsilon \neq 0$ are then $\Delta J = 1$, $\Delta K = 0$, $\Delta M = \pm 1$. By rotating the input/output waveguide couplings through 90°, the two electric vectors become parallel and only $\Delta M = 0$ transitions are allowed.

The gas mixture was pulsed into the Fabry–Pérot cavity through a circular nozzle of 0.7 mm diameter and consisted of $\approx 2\%$ each of PH₃ and HC¹⁵N in argon held at ≈ 1 atm pressure and room temperature. HC¹⁵N was prepared by the action of H₃PO₄ (to which P₂O₅ had been added) on KC¹⁵N (Amersham International plc) in vacuum. The reaction of aluminium phosphide with 6 M sulphuric acid was used to generate PH₃ which was dried first by vacuum distillation at -50°C and then with P₂O₅. The effective separation of the parallel Stark plates was calibrated by measuring the $|M| = 1 \leftarrow 1$ components of the $J = 2 \leftarrow 1$, K = 1transition of (CH₃)₃CC=CH (supplied by Aldrich Chemical Co.), for which $\mu = 0.664(4)$ D [4]*.

3. Results

We chose the $J = 4 \leftarrow 3$, K = 1 transition of H₂P...HC¹⁵N as the subject of the first attempt to observe the Stark effect with our pulsed-nozzle FT microwave spectrometer for two reasons. First, the dimer has been shown to be a symmetric-top molecule of C_{3v} symmetry [6] and therefore the transition will exhibit a first-order Stark effect. Appreciable Stark shifts can then be observed at very small electric field strengths, with the consequence that large separations d of the parallel plates can be used with small potential differences V. The larger the value of d, the smaller will be the perturbing effect of the metal plates on the molecules in the gas pulse and on the Q of the cavity. Moreover, a small potential difference between the plates eliminates the possibility of an electrical discharge through the gas. Secondly, our choice of the isotopic species H₂P...HC¹⁵N is advantageous because the $J = 4 \leftarrow 3, K = 1$ transition at zero field is a singlet (i.e. a doublet when observed with this spectrometer)

with no resolvable hyperfine structure. This ensures that the Stark effect is simple and can be interpreted unambiguously.

The first-order correction $W_{JKM}^{(1)}$ to the rotational energy of a state $|J_K\rangle$ of a symmetric-top molecule in the presence of a uniform static electric field of strength ϵ is given by

$$\mathcal{W}_{JKM}^{(1)} = -\mu \epsilon M K / J (J+1), \qquad (1)$$

where μ is the electric dipole moment of the molecule and the quantum numbers J, K and M have their usual meanings. For an experiment where the selection rule is $\Delta M = 0$, the shifts in frequency of the allowed transitions from the zero-field are

$$\Delta \nu_0 = 2\mu \epsilon K M / h J (J+1) (J+2) \tag{2}$$

but if the selection rule is $\Delta M = \pm 1$, the corresponding shifts are

$$\Delta \nu_{\pm 1} = \mu \epsilon K (2M \mp J) / h J (J \pm 1) (J \pm 2).$$
(3)

At the values of μ and ϵ discussed here, the secondorder Stark effects are negligible.

Eq. (2) shows that in the applied electric field the $J = 4 \leftarrow 3, K = 1$ transition of H₃P...HC¹⁵N should split into 7 components, forming a symmetrical pattern with frequency shifts (in units of $\mu \epsilon/60h$) of 0, ±2, ±4 and ±6. This effect is clearly evident in fig. 1 which was recorded at $\epsilon \approx 2 \text{ V cm}^{-1}$ and shows the M = 0component at the unshifted frequency $v_0 = 12070.5413$ MHz together with one half of the symmetrical pattern. The stick diagram represents the calculated spectrum, for which the theoretical relative intensities are 16: 15: 12:7 for the |M| = 0, 1, 2 and 3 components, respectively. Fig. 1 was recorded with the broad face of the input/output waveguide couplings vertical so that the electric vectors of the static field and radiation in the cavity are parallel and selection rule $\Delta M = 0$ is appropriate.

When the input/output waveguide couplings are rotated through 90°, $\Delta M = \pm 1$ instead of $\Delta M = 0$ transitions are allowed. The result of doing this for an electric field strength $\epsilon \approx 1$ V cm⁻¹ is shown in fig. 2. According to eq. (3), we expect a symmetrical pattern with frequency shifts (in units of $\mu e/60h$) of $\pm 1, \pm 3, \pm 5, \pm 7$ and ± 9 . The calculated relative intensities of the transitions are 36: 38: 6:3:1, in the order given. In experiments reported here, only the two strong, inner pairs of transitions were measured and in fact only

^{*} The value $\mu = 0.661(4)$ D in ref. [4] has been multiplied by 0.71521/0.7124 to allow for the revised value of the electric dipole moment of OCS [5].



Fig. 1. The first-order Stark effect allowed by the selection rule $\Delta M = 0$ in the $J = 4 \leftrightarrow 3$, $K_{i} = \sqrt{1}$ transition of H₃P...HC¹⁵N recorded with an applied electric field strength $\epsilon \approx 2.0$ V cm⁻¹ by means of a pulsed-nozzle, FT microwave spectrometer. In this power spectrum, obtained by Fourier transformation of a time domain recorded at a digitization rate of 0.5 μ s/point, frequencies are offset at a rate of 3.90625 kHz/point from $\nu = 12071.0600$ MHz. The stick diagram gives the calculated pattern and the M = 0 component occurs at the unshifted frequency $\nu_0 = 12070.5413$ MHz.

these are evident in fig. 2. Nevertheless, fig. 2 demonstrates clearly the symmetrical nature of the $\Delta M = \pm 1$ first-order Stark effect with respect to ν_0 , the position of which is indicated. The relative intensities in fig. 2 are incorrect because the cavity is deliberately tuned to ν_0 and its high Q discriminates against transitions with larger shifts from ν_0 .

Table 1 gives the measured first-order Stark shifts for a range of applied potentials V for both $\Delta M = 0$ and $\Delta M = \pm 1$ transitions. We estimate that these shifts have an accuracy of 3 kHz or better. We demonstrate in fig. 3 that for each Stark component observed under either $\Delta M = 0$ or $\Delta M = \pm 1$ selection rules, $\Delta \nu$ is indeed directly proportional to V, as expected from eqs. (2) and (3). Moreover, the pattern of the straight lines in fig. 3 is symmetrical with respect to the abscissa, confirming that second-order effects are negligible. The set of ($\Delta \nu$, V) values for each Stark component given



Fig. 2. The first-order Stark effect allowed by the selection rule $\Delta M = \pm 1$ in the $J = 4 \leftrightarrow 3$, K = 1 transition of H₃P...HC¹⁵N recorded with an applied electric field strength $\epsilon \approx 1.0 \text{ V cm}^{-1}$ by means of a pulsed-nozzle, FT microwave spectrometer. Frequencies are offset at a rate of 3.90625 kHz/point from $\nu = 12070.7400$ MHz. The stick diagram gives the calculated pattern. The position of $\nu_0 = 12070.5413$ is indicated. Observed relative intensities are unreliable (see text).



Fig. 3. Frequency shifts plotted against potential difference applied to the parallel plates (separation d = 20.45 cm) for the $\Delta M = 0$ and $\Delta M = \pm 1$ first-order Stark components of the $J = 4 \leftarrow 3$, K = 1 transition of H₃P...HC¹⁵N.

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Transition	Observed frequency shifts $\Delta \nu$ (kHz) at potential diff. $V(V)$					μ(D)
	V = 20	40	60	80	100	
$\Delta M = 0$						
$M = -2 \leftarrow -2$	-120.8	-258.8	391.5	-524.7	-	4.094(56)
$M = -1 \leftarrow -1$	-65.6	-129.5	-196.8	-261.4	-	3.984(56)
$M = 1 \leftarrow 1$	67.5	132.9	199.8	263.4		3.984(55)
$M = 2 \leftarrow 2$	126.1	260.3	392.2	527.6	_	4.069(44)
$\Delta M = \pm 1$	-					
$M = \begin{cases} 1 \leftarrow 0 \\ -4 \leftarrow -3 \end{cases}$	-91.1	-190.0	-294.0	-391.9	490.2	4.061(56)
$M = \left\{ \begin{array}{c} 2 \leftarrow 1 \\ -3 \leftarrow -2 \end{array} \right\}$	-35.9	-67.8	-97.9	132.6	-165.3	3.947(79)
$M = \left\{ \begin{matrix} 3 \leftarrow 2 \\ -2 \leftarrow -1 \end{matrix} \right\}$	38.6	70.5	103.9	136.1	167.6	3.943(53)
$M = \left\{ \begin{array}{c} 4 \leftarrow 3 \\ -1 \leftarrow 0 \end{array} \right\}$	94.6	194.8	296.7	395.9	495.2 weighted mean ^{a)}	4.069(40)

Table 1 Observed first-order Stark shifts in the $J = 4 \leftarrow 3$, K = 1 transition of H₃P...HC¹⁵N

a) Values from $|M| = 2 \leftarrow 1, 3 \leftarrow 2$ pair excluded. See text for discussion.

in table 1 was fitted with the aid of the appropriate equation (2) or (3) and the least-squares method to give a value of the electric dipole moment of H₃P...HC¹⁵N, with the results shown in table 1. In each case, the standard deviation of the fit was 1 kHz or less, which is satisfactory. We calculated the electric field strength ϵ from V by using the effective parallel plate separation d = 20.45(16) cm, a value determined by measuring the frequency shifts of the $|M| = 1 \leftarrow 1$ components in the $J = 2 \leftarrow 1$, K = 1 transition of the symmetric top molecule $(CH_3)_3CC \equiv CH$ for which the electric dipole moment is accurately known (ref. [4] and see section 2). This method of calibration is convenient because, for a given V, the Stark shifts of the transition are of similar magnitude to those observed in the $J = 4 \leftarrow 3$, K = 1 transition of H₃P...HC¹⁵N. The more familiar calibrants, such as OCS and propyne, are unsatisfactory because only their $J = 1 \leftarrow 0$ transitions fall within the frequency range of our spectrometer and unfortunately these exhibit second-order Stark effects which are negligibly small at the ϵ values used here. The actual separation of the parallel plates (measured by calipers) was 19.97(1) cm. The difference from 20.45(16) cm gives an indication of the non-uniformity of the field.

We note in table 1 that while the μ values determined

from six of the Stark components are identical within one standard deviation, those arising from the two $|M| = 3 \leftarrow 2, 2 \leftarrow 1$ components are slightly lower. We recognise, however, that these two components have the smallest Δv at any given V (see fig. 3 and table 1) and also that the straight lines associated with them in fig. 3 do not intercept at the origin. The error in μ determined from one of these components is, moreover the largest of the set, as might be expected (we believe that the error for the other is fortuitously low). In view of the foregoing, we have excluded the μ values generated from the $|M| = 3 \leftarrow 2, 2 \leftarrow 1$ components in arriving at the weighted mean value given in table 1.

4. Discussion

The observed value for the electric dipole moment of H₃P...HC¹⁵N in its vibrational ground state is $\mu =$ 4.046(47) D. We have shown previously [6] that the equilibrium conformation of this dimer is of C_{3v} symmetry, with HCN forming a hydrogen bond to the P atom in PH₃. As discussed in ref. [6], a suitable model for the zero-point motion in the dimer consists of the oscillation of the two rigid subunits about respective centres of mass, as defined by the angles θ and ϕ



Fig. 4. Model of H₃P...HC¹⁵N used in the determination of the electric dipole moment enhancement $\Delta \mu$ from μ , μ PH₃ and μ HCN-

for H₃P and HCN, respectively, in fig. 4. It is assumed that the distance between the two mass centres remains fixed during the motion. The zero-point electric dipole moment of H₃P...HC¹⁵N can then be expressed in terms of the corresponding values of $\mu_{\rm PH_3}$ and $\mu_{\rm HCN}$ of the components by

$$\mu = \mu_{\text{PH}_3} \langle \cos \theta \rangle + \mu_{\text{HCN}} \langle \cos \phi \rangle + \Delta \mu , \qquad (4)$$

where angular brackets denote an average over the zero-point state and $\Delta \mu$ accounts for any changes in μ_{PH_2} and μ_{HCN} that occur as a result of formation of the dimer. We do not have values of $\langle \cos \phi \rangle$ and $\langle \cos \theta \rangle$ but $\langle \cos^2 \phi \rangle = 0.9504$ is available [6] from an interpretation of the ¹⁴N-nuclear quadrupole coupling constant in H₃P...HC¹⁴N. If we assume that $\langle \cos \phi \rangle \approx \langle \cos^2 \phi \rangle^{1/2}$ because ϕ is small and if we take $\langle \cos \theta \rangle \approx \langle \cos^2 \theta \rangle^{1/2} = 0.9373$ from the analogous H₃N...HCN [7], we obtain the value $\Delta \mu = 0.60$ D when the zero-point electric dipole moments $\mu_{\text{PH}_3} = 0.57395 \text{ D} [8] \text{ and } \mu_{\text{HCN}} = 2.985 \text{ D} [9] \text{ are}$ used in eq. (4). If H is the positive end of the HCN dipole, our use of eq. (4) provides evidence that P is the negative end of the H₃P dipole, given the known [6] order H₃P...HCN of the nuclei. Use of the opposite sign for μ_{PH_3} results in the unreasonably large value $\Delta \mu = 1.67$ D.

Finally, we comment on the fact that the Doppler doubling effect is not apparent in the Stark components shown in figs. 1 and 2, except for the $M = 0 \leftarrow 0$ component of fig. 1. The doubling occurs in all zero field transitions investigated by pulsed-nozzle, Fouriertransform microwave spectroscopy and arises from the distribution of the molecules in the emitting gas pulse coupled with the fact that the Fabry-Pérot cavity is a standing wave device [10]. Our Stark plates are relatively small and presumably only in the central region between the plates is the electric field truly homogeneous. Molecules outside this region will suffer a wide range of electric field strength as a result of edge effects. Accordingly, the emission signal from molecules outside the central region will be spread thinly over a wide range of frequencies and lead to an essentially undetected background. Effectively, therefore, we discriminate in favour of molecules in the central region and collect a substantial coherent emission signal from these alone. But molecules in the central region will be those that are travelling close to the nozzle-diffusion pump axis and nearly perpendicular to the cavity axis. For such molecules, the Doppler effect is smaller and presumably unresolved. Of course, for the $M = 0 \leftarrow 0$ component the Stark coefficient is zero and the above discrimination does not occur. Campbell et al. [11] used Stark plates of much larger area than ours when applying electric fields to molecules in the expanded gas pulse. They observed a welldefined doubling, presumably because the larger plates lead to proportionally smaller edge effects.

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