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Avoided Crossings in Molecular-Beam Electric-Resonance Spectroscopy: The Observation of Forbidden ($\Delta K = \pm 1, \pm 2, \pm 3$) Transitions in Phosphoryl Fluoride (OPF_3)

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Normally forbidden transitions obeying the selection rules $\Delta K = \pm 1, \pm 2$, and ± 3 have been observed in OPF_3 in the ground vibronic state by a new avoided-crossing technique based on the molecular-beam electric-resonance method. It is shown how this technique can be used in suitable symmetric rotors to study the K-dependent terms in the rotational Hamiltonian, the effects of centrifugal distortion on the total electric dipole moment, and the nuclear hyperfine effects off-diagnoal in K.

A new avoided-crossing technique based on the molecular-beam electric-resonance (MBER) method is reported with which transitions following the selection rules $\Delta K = \pm 1, \pm 2$, and ± 3 have been studied in the symmetric top phosphoryl fluoride (OPE_3) in the ground vibronic state.

These transitions are normally forbidden[1] because the permanent electric dipole moment $\vec{\mu}$ lies along the symmetry axis. In the $\Delta K = \pm 1$ and ± 2 transitions, the symmetry of the rotational wave function changes, and, in some cases, ortho-para conversion occurs between different fluorine nuclear spin states. No transition of this type has been previously reported for a symmetric rotor.

Using this technique, it is possible in favorable cases to study three problems of current interest that can otherwise be investigated only with considerable difficulty, if at all. First, one can obtain the rotational constant A_0, which is very important in the determination of molecular structure. Secondly, one can study in detail centrifugal distortion effects on the total electric dipole moment. These effects cause the parallel moment μ to take the form $\mu_0 - J(J+1)\mu_J - K^2\mu_K$ and generate[2] a perpendicular component μ_D. Except for a small correction, μ_0 is the equilibrium parallel moment, while μ_J, μ_K, and μ_D can be related to Watson's distortion dipole tensor $\theta_\alpha{}^{\beta\gamma}$.[3] Thirdly, one can investigate the nuclear hyperfine terms which are off diagonal in K. These terms can play an important role in the equilibration of interstellar molecules[4] and in the density dependence of the nuclear spin-lattice relaxation time.[5]

If all terms off diagonal in K are neglected, the energy E of an OPF_3 molecule in a large external field $\vec{\mathcal{E}}$ can be written as $E_{ROT} + E_S + E_{HYP}$. To lowest order, the rotational term $E_{ROT} = B_0 J \times (J+1) + (A_0 - B_0)K^2$. The rotational constant $B_0 = 4594.2624(4)$ MHz.[6] The Stark term $E_S = -\mu\mathcal{E} \times m_J K / J(J+1)$, where m_J is the eigenvalue of the component of $\vec{J}$ along $\vec{\mathcal{E}}$. The other magnetic quantum numbers are m_P and m_F for the phosphorus and total fluorine spins, respectively. $m_T \equiv m_J + m_P + m_F$. The nuclear hyperfine term E_{HYP} makes only a small contribution to E.[7]

Consider a pair of levels with different K such that the state of larger E_{ROT} has a negative Stark effect while that of smaller E_{ROT} has a positive Stark effect. If the levels are coupled and have the same m_T, then they can be made to undergo an avoided crossing by varying $\mathcal{E}$. Near the crossing field $\mathcal{E}_C$ at which the levels have their minimum energy difference ν_m, the states are thoroughly mixed and $\Delta m_T = 0$ transitions between them are easily driven through μ. Furthermore, because of the change in the sign of the Stark effect, the transitions meet the conditions for detection[8] imposed by the flopout alignment of the quadrupole deflection fields commonly used in MBER machines. From $\mathcal{E}_C$, the zero-field splitting E_0 can be obtained; from ν_m, the magnitude of the mixing term can be determined. The crossings detected for OPF_3 in the $J = 2$ state are indicated in Fig. 1.

For the $\Delta K = \pm 3$ cases, referred to here as "Stark crossings," the mixing is provided by the Stark Hamiltonian W_S' associated with μ_D. Since W_S' is diagonal in m_J, $\mathcal{E}_C = [(A_0 - B_0)/\mu] J(J+1) \times |(2k+3)/m_J|$ to lowest order. Here K is the algebraically smaller of the two values involved. Because W_S' is also diagonal in m_F and m_P, only the K-dependent terms in E_{HYP} can affect $\mathcal{E}_C$. If their variation with m_P and m_F is small compared with the instrumental linewidth, only the average

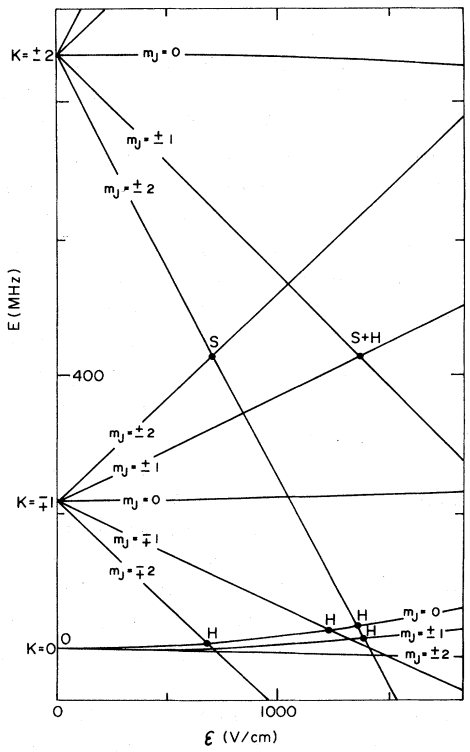

FIG. 1. Avoided Stark crossings (S) and avoided hyperfine crossings (H) observed in the $J = 2$ state of OPF_3. Because ν_m is so small, the energy levels are drawn as though they actually cross. For clarity, the quadratic Stark effect of the levels with K and/or $m_J = 0$ has been greatly exaggerated. F_{HYP} and the nuclear-spin quantum numbers have been omitted. All the levels (except $K = m_J = 0$) are doubly degenerate. In spite of this, all the crossings can be treated as a problem of two interacting levels, except that labeled "S + H." This is a multilevel problem involving both Stark and hyperfine mixing.

over m_P and m_F is relevant, and this average vanishes.

For the $\Delta K = \pm 1$ and $\Delta K = \pm 2$ cases, referred to here as "hyperfine crossings," the mixing is provided by the hyperfine terms[9] W_{HYP}' off diagonal in K. Both selection rules are met by the F-F and F-P dipolar interactions. The c_{yz} and $c_{xx}-c_{yy}$ fluorine spin-rotation terms meet the $\Delta K = \pm 1$ and $\Delta K = \pm 2$ selection rules, respectively.[10] In conventional spectroscopy, c_{yz} does not enter, while $c_{xx}-c_{yy}$ enters only when $K = \pm 1$ and is very difficult to extract. Both the dipolar and the spin-rotation terms can be off diagonal in the magnetic quantum numbers. Consequently E_{HYP} makes a direct contribution to $\mathcal{E}_C$. This is equivalent to $\lesssim 10$ kHz in E_0 for OPF_3. For any specific crossing, $\mathcal{E}_C$ can be calculated to lowest order from the expressions above for E_{ROT} and E_S. $\mathcal{E}_C$ takes its minimum value of $2(A_0-B_0)/\mu$ for $J=1$, $m_J = \pm 1 \rightarrow 0$, $K = \pm 1 \rightarrow 0$.

The basic MBER apparatus used here has been described elsewhere.[11] The beam was formed by passing a mixture of 4% OPF_3 in argon through a room-temperature jet source with a nozzle diameter of 20 μm and a backing pressure of 1 atom; the rotational temperature in the beam was ~ 6 K.[12] The resulting concentration of the molecules in the lower J states was essential because A_0 and B_0 are so small. The line shape was symmetric and had a full width $\Delta\nu$ at half-maximum of 18 kHz. For the strongest lines, a signal-to-noise ratio of 40 was obtained in a single scan with a time constant of 1 sec. The values of the crossing voltages fell in the range 250 to 1800 V. The transition frequencies fell in the range 60 to 10 000 kHz. For calibration purposes, it was determined that $\mu/d = 2.936\,318(59)$ D/cm, where d is the separation of the C-field plates. This was done using the normal MBER transtions ($J=3, K=2, m_J=0) \rightarrow (3,2,-1)$ and $(2,1,0) \rightarrow (2,1,-1)$.

The Stark crossings were studied first. To determine A_0-B_0, $\mathcal{E}_C$ was measured for the $K = \mp 1 \rightarrow \pm 2$ crossings with $m_J = J$ for $J = 2$–6. In each case, lines were measured above and below the crossing for both polarities of the voltage. To minimize the correlation with ν_m, all four frequencies for each crossing were approximately the same and were $> 10\nu_m$. From each $\mathcal{E}_C$, E_0 was calculated by diagonalizing the rotational and Stark matrices truncated so that $\Delta J \leq 3$. In E_{ROT}, the quartic distortion constants were taken into account with $D_{JK} = 1.2971(7)$ kHz and $D_K = -1.114(12)$ kHz.[13] μ/d was taken to be constant. The term in μ_K is not important because it is the same for all $K = \mp 1 \rightarrow \pm 2$ crossings. The contribution from μ_J was then calculated by a simple correction procedure.

Because the accuracy for μ_J was severely limited by the long-term stability (2×10^{-5}) of the voltage source, a second set of measurements was taken. Two $K = \mp 1 \rightarrow \pm 2$ crossing transitions were observed in the same $\mathcal{E}$ for different J, so that only the short-term stability (2×10^{-6}) of the voltage V enters. Furthermore, the linear Stark coefficients for the frequencies in the pair were identical except for the μ_J term, so that the fractional contribution of μ_J was greatly increased. Such relative measurements were made for four pairs of crossings including ($J=3$, $m_J=1$) with ($J=8$, $m_J=6$). It was determined that $\mu_J = 3.28(13)\times10^{-6}$ D as compared with $\mu_0 = 1.868\,47(10)$ D obtained[14] from the normal spectrum. The power of the current technique is illustrated by the fact that $\mu_J/\mu_0 \sim 2\times10^{-6}$. It was also found that $A_0-B_0 = 217\,494(4)$ kHz, where the absolute error is determined by the uncertainty in μ/d.

For a $K = \mp 1 \rightarrow \mp 2$ crossing with $m_J = J$, $\nu_m = \mu_D \mathcal{E}_0 J[(J-1)(J+2)]^{1/2}$. For $J \geq 4$, ν_m was large enough relative to $\Delta\nu$ that the transition frequency could be measured accurately right through the avoided crossing. This was done for $J=4$ and 6. The values obtained for μ_D were $5.835(67)\times10^{-6}$ D and $5.858(20)\times10^{-6}$ D respectively. The two agree well. μ_D is of the same order as μ_J. The current measurements of μ_J *and* μ_D are the *first* to be carried out for a symmetric top.[15]

Six hyperfine crossings[16] were studied: the four shown in Fig. 1 along with ($J=1$, $K = \pm 1 \rightarrow 0$, $m_J = \pm 1 \rightarrow 0$) and ($J=3$, $K = \pm 3 \rightarrow \pm 2$, $m_J = \pm 1 \rightarrow \mp 1$). To calibrate V, a Stark crossing was measured at the same V for each hyperfine case except $J=1$ for which no reference was available. These data are currently being analyzed along with the conventional MBER spectrum to extract the hyperfine constants and μ_K. For all the hyperfine crossings in OPF_3, ν_m was too small to be measured directly, but work is underway to determine ν_m from the rf voltage required to optimize the transition probability.

When a magnetic field $\vec{H}$ is applied parallel to $\vec{\mathcal{E}}$, each avoided-crossing line splits into one or more pairs of lines. For the splitting between members of a pair, the effective g factor is $g_{eff} = 2\Delta m_F g_F + 2\Delta m_P g_P + g_{MOL}$. For the Stark crossings, g_{eff} reduces to g_{MOL}, which depends on the specific transition but arises only from the molecular g factor. For OPF_3, g_{MOL} is so small

that the splitting was not resolved. For the hyperfine crossings, the fluorine and phosphorus g factors, g_F and g_P, respectively, enter as well and splittings of several megahertz were obtained for $H \lesssim 1000$ G. For each hyperfine crossing, g_{eff} was measured for each pair detectable and the dominant selection rules on m_F and m_P were established. Furthermore, it was determined that the molecular g factors are negative. These signs are usually very difficult to obtain by other techniques. The H dependence of the transition frequencies can be used to assist in the determination of the hyperfine constants.

This initial avoided-crossing experiment was done on OPF_3 primarily because $(A_0 - B_0)/\mu$ is small and a reliable value for $A_0 - B_0$ was available.[13a] However, the current work shows that a wide range of symmetric tops such as CF_3H with $A_0 - B_0 \sim 5$ GHz and $\mu \sim 1$ D can be studied. Electric fields of the necessary magnitude and homogeneity to measure $A_0 - B_0$ can be generated and the signal-to-noise ratio is so good that wide searches can be carried out rapidly.

For many of the molecules whose A_0 can be measured by the present technique, there is no alternative method currently available. For OPF_3, distortion moment spectroscopy has indeed yielded $A_0 - B_0 = 217\,495(2)$ kHz,[13b] in excellent agreement with the present value. However, this microwave technique requires a relatively large μ_D, can be applied only to high-J states, and for heavy tops faces[13] a significant assignment problem. By contrast, the MBER method will work for very small μ_D. It can be applied only to low-J states, but faces no serious identification problems. Where both methods work, as in the OPF_3, the MBER data can be used to resolve any ambiguities in the microwave assignments. Both methods require a small or moderate $A_0 - B_0$, but can be applied to heavy molecules with very complicated energy levels in the excited vibrational states. Again, in contrast, the combination-differences method using perturbation-allowed infrared transitions[17] is not limited directly by the value of $A_0 - B_0$, but has to date worked only for light molecules with much simpler vibration-rotation spectra. The same comment applies to the Raman technique recently developed,[18] but the accuracy is not yet as high as in the other methods.

Work is underway to refine the present measurements on OPF_3 and to apply this technique to other symmetric tops, including some with internal rotation. For systems of this type, it should be possible to determine the barrier height, a very important molecular parameter which has not previously[1] been obtained to high accuracy in a symmetric rotor. A full report of the current work will be published elsewhere.

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