New Method of Studying Internal Rotation in a Symmetric Rotor

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A technique has been developed for the first time to study the internal rotation splittings in the ground torsional state of a symmetric rotor. Normally forbidden transitions obeying the selection rules $\Delta K=\pm1,\pm2,\pm3$ and $\Delta\sigma=0,\pm1$ have been observed in an avoided-crossing experiment using molecular-beam electric-resonance spectroscopy. For CH_3CF_3, it has been found that the barrier height $V_3=3.16(11)$ kcal/mol and the moment of inertia I_α of the methyl top is 3.17(11) amu Å^2.

Internal rotation has long been an important subject in molecular physics.[1,2] Although the underlying physical concepts are well understood, a satisfactory theory accounting in detail for the height of the hindering barrier has not been developed[3,4] and the semiempirical models[5] for the interaction between internal rotation and ordinary vibration have been only partially tested.[4] Precision data on barrier heights are available only for asymmetric rotors where the splittings due to the interaction of internal and overall rotation can be measured with conventional microwave spectroscopy.[1,2] The detailed interpretation of these results is, however, very difficult because of the complexity of the relevant energy expressions. For a symmetric top, these expressions are very simple, but the ($\Delta K=0$) selection rule[2] for normal electric-dipole transitions eliminates the splittings from the transition frequencies and other techniques must be used whose ultimate accuracy is much lower.[6]

In the current work, there is developed a precision method of measuring the torsional splittings that can be applied to a number of symmetric tops of C_{3v} symmetry, thereby opening the way for studying internal rotation with very high resolution in some of the simplest possible systems and obtaining a more detailed understanding of the origins of the barrier. The technique has been applied to CH_3CF_3 to determine the height V_3 of the threefold barrier and the moment of inertia I_α of the methyl top about its symmetry axis.

The method is based on the avoided-crossing technique recently developed[7] for molecular-beam electric-resonance (MBER) spectroscopy. In OPF_3, transitions were observed[7] following the selection rules $\Delta J=0$, $\Delta K=\pm3$, $\Delta m_J=0$ at "Stark crossings" and $\Delta J=0$, $\Delta K=\pm1,\pm2$, $\Delta m_J=\pm1,\pm2$ at "hyperfine crossings." m_J is the magnetic quantum number for $\vec{J}$. In CH_3CF_3, the quantum number σ is introduced to specify the symmetry of the torsional wave function: $\sigma=0$ and ±1 refer, respectively, to the A and E states. In the current work, the selection rules on σ were found experimentally to be $\Delta\sigma=0$ at Stark crossings and $\Delta\sigma=0,\pm1$ at hyperfine crossings. For $\Delta\sigma=\pm1$, the symmetry of the torsional wave function changes. To our knowledge, no such transitions have been previously observed.

For CH_3CF_3 in free space in the ground vibronic state, the energy E_0 which depends on J and K is dominated by $E_{\rm rot}$ and $E_{\rm int}$. The pure rotational term[2] is

$$E_{\rm rot}=B_0J(J+1)+(A_0-B_0)K^2-D_JJ^2(J+1)^2-D_{JK}K^2J(J+1)-D_KK^4.$$

$E_{\rm int}$ arises from the interaction between overall and internal rotation. In the internal-axis method (IAM),[1] we have

$$E_{\rm int}(J,K,\sigma)=a_1F[1-2\pi^2\rho^2K^2/9][1-3\sigma^2/2]+a_1F\pi\sigma\rho K/\sqrt{3}\ . \quad (1)$$

Here $\rho=I_\alpha/I_Z$ where I_Z is the moment of inertia of the molecule about the symmetry axis, $F\equiv A_0/\rho(1-\rho)$ is the reduced rotational constant for internal rotation, and a_1 is the coefficient of the leading cosine term[1] in the IAM expansion of $E_{\rm int}$. a_1 depends only on the reduced barrier height $s\equiv4V_3/9F$. For $n>1$, a_n is negligible because s is so large ($s\sim89$). The cosine has been expanded and terms in $(\rho K)^j$ with $j>2$ have been omitted because only low value of K enter and ρ is small ($\rho\sim0.035$). The torsional quantum number has been suppressed because only the ground torsional state is of interest here. A third energy term $E_{\rm hyp}$ due to nucelar hyperfine interactions must also be included, although its effects are much smaller ($\lesssim20$ kHz).

To apply the avoided-crossing technique, an external electric field $\vec{\mathcal{E}}$ is introduced. Two levels are selected with different K but the same magnetic quantum number for the total angular

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momentum. The two Stark effects must have opposite signs. $\mathcal{E}$ is set close to the value $\mathcal{E}_C$ at which the difference in the zero-field energies is exactly canceled by the difference in the Stark energy arising from the normal dipole moment μ along the symmetry axis. In calculating the contribution of $E_{\rm hyp}$ to E_0, the strong-field representation[1] must be used. At Stark crossings, for $\mathcal{E} \sim \mathcal{E}_C$, the two levels are strongly mixed by the distortion dipole moment μ_D,[7,8] and the normally forbidden transitions can be observed. At hyperfine crossings, the mixing is provided by nuclear hyperfine terms.[9,10]

Because of $E_{\rm int}$, there exist families of related crossings; the family is indentified by the values of J, K, K', m_J, and m_J' and the individual members are specified by σ and σ' if $E_{\rm hyp}$ is neglected. For the Stark crossings, $E_{\rm hyp}$ is indeed negligible at the resolution used here and each family consists of three crossings as can be shown from Eq. (1) and is illustrated in Fig. 1(a). If the spectrum is observed for $\mathcal{E} < \mathcal{E}_C$ at frequencies large compared to the minimum splittings between pairs of interacting levels, then the *normal* spectrum is observed, i.e., the splittings equal the zero-field values. In the *normal* Stark crossing spectrum, there are three lines whose frequencies, in order of increasing magnitude, are labeled ν_{-1}^S, ν_0^S, and ν_{+1}^S corresponding, respectively, to $\Delta(K\sigma) = +3$, 0, and -3. The splitting between outer members of the triplet is $\delta \equiv (\nu_{+1}^S - \nu_{-1}^S) = -2\pi\sqrt{3}\,F\rho a_1 \simeq 100$ kHz here. The pattern is slightly asymmetric; $\delta_a \equiv (\nu_0^S - \nu_{-1}^S) - (\nu_{+1}^S - \nu_0^S) = \rho(\pi/\sqrt{3})\,\delta = 6$ kHz for CH_3CF_3.

For the hyperfine crossings, $E_{\rm hyp}$ is initially neglected. As can be shown from Eq. (1) and is illustrated in Fig. 1(b), each family of crossings breaks up into three groups. In the normal spectrum, there are three groups of lines whose *average* frequencies, in order of increasing magnitude, are labeled ν_{-1}^H, ν_0^H, and ν_{+1}^H corresponding, respectively, to $\Delta|\sigma| = -1$, 0, and $+1$. The splitting between the outer groups is $\Delta \equiv \nu_{+1}^H - \nu_{-1}^H = -3a_1F + a_1F\rho^2(\pi^2/3)(K^2 + K'^2) = 870$ kHz for CH_3CF_3. Each group is split internally, primarily by the term linear in K in Eq. (1). If $E_{\rm hyp}$ is

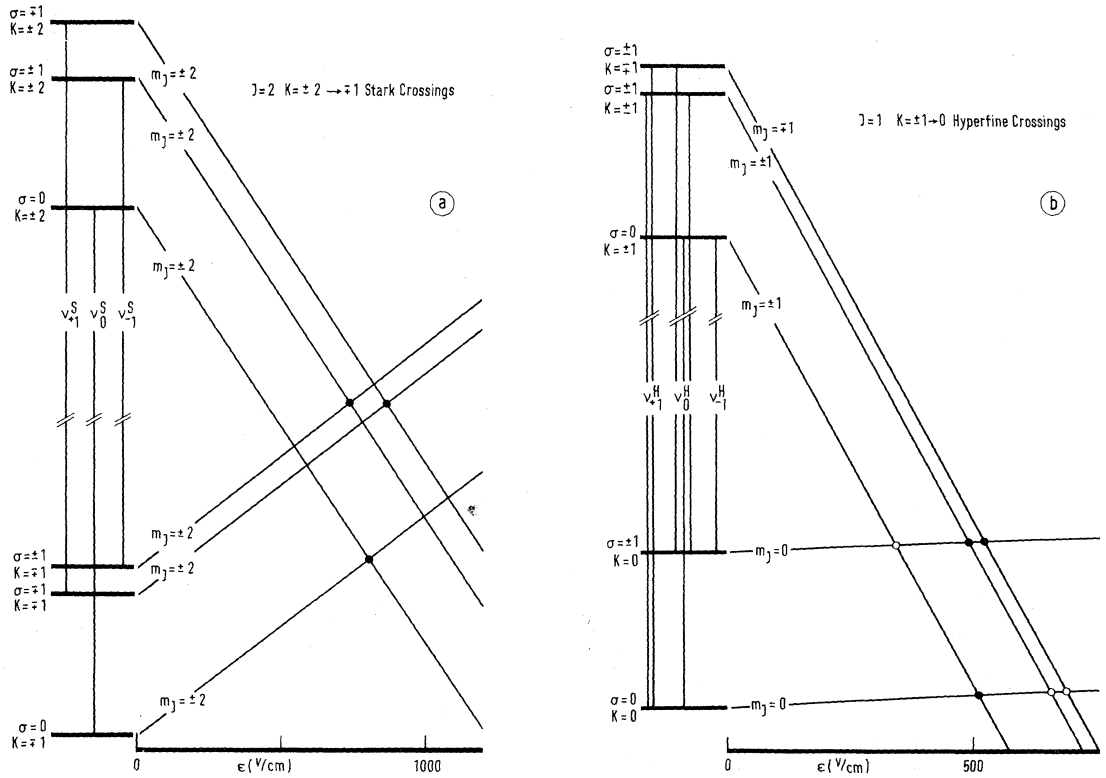

FIG. 1. Torsion-rotation energy level diagram and avoided crossings with mixing due to (a) distortion dipole moment and (b) nuclear hyperfine effects. Level crossings with $\Delta\sigma = 0$ and ± 1 are indicated, respectively, by solid and open circles. For clarity, the energies are not to scale and only those levels relevant for the crossings are drawn. Upper- (lower-) sign levels interact with upper- (lower-) sign ones.

taken into account, additional splittings can occur within each group and the average frequencies can be shifted. We take ±30 kHz to be a conservative upper limit to the contribution of $E_{\rm hyp}$ to Δ. As is shown below, ρ and s can be calculated from Δ and δ.

Two preliminary experiments were done. First, the R-branch spectra for $J=8\rightarrow 9$, $9\rightarrow 10$, and $10\rightarrow 11$ were observed with a millimeter-wave spectrometer[11] operating in the 100-GHz region. The splittings due to D_{JK} were clearly resolved for $K\geq 5$. It was found that $B_0 = 5185.1387(24)$ MHz, $D_J = 1.267(11)$ kHz, and $D_{JK} = 2.006(14)$ kHz. The result for B_0 agrees with the earlier, less accurate microwave value[12]; the distortion constants have not been previously reported. Second, from the conventional MBER spectrum, a preliminary value of 2.3470(5) D was obtained for μ.

The MBER spectrometer used has been described elsewhere.[13] The operating conditions and procedures for studying crossing spectra were similar to those used for OPF_3.[7] The line shape had a full width at half-maximum of 18 kHz. The signal-to-noise ratio for the strongest lines was 10 with a time constant of 1 sec.

The Stark crossings $(J, K=\mp 1, \sigma, m_J) \leftrightarrow (J, K=\pm 2, \sigma, m_J)$ were studied for $J=2$, 3, and 6. By methods described earlier,[7] it was found that $A_0 - B_0 = 313.711(70)$ MHz and $A_0 = 5498.850(70)$ MHz. The contribution of D_K was not eliminated but is negligible, being $\lesssim 10$ kHz. The error in $A_0 - B_0$ can be reduced to ~4 kHz once the final value of μ is obtained and D_K is measured. For each of the three J states, $\nu_{-1}^{\,S}$, $\nu_0^{\,S}$, and $\nu_{+1}^{\,S}$ were determined. The splittings were independent of J to within the experimental error of ~0.8 kHz. It was found that $\delta = 108.8(8)$ kHz. With the value of ρ given below, it was determined that $a_1 = -1.756(13)\times 10^{-6}$ and $s = 89.22(9)$. Because $\rho \ll 1$, $F\rho = A_0/(1-\rho)$ is insensitive to ρ and s is not significantly correlated to ρ.

Five hyperfine crossings for $J=1$ and $J=2$ were studied. In each case, Δ was measured: The average was 867 kHz and the total spread was < 50 kHz. From the definitions of Δ and δ, we have

$$1/\rho = (2\pi/\sqrt{3})(\Delta/\delta) + (\pi^2\rho/9)(K+K'^2). \qquad (2)$$

ρ was obtained for all five crossings; the mean is 0.0345(12) where the error is due to the ±30-kHz uncertainty assigned to Δ because of $E_{\rm hyp}$. *Because a_1 does not appear in Eq. (2), this result is independent of s.* From ρ and A_0, $I_\alpha = 3.17(11)$ amu Å^2 which is in good agreement with the values[1,2,14] obtained for methyl tops in asymmetric rotors. From ρ, s, and A_0, $V_3 = 3.16(11)$ kcal/mol, where the error is entirely due to the contribution from ρ. This result is in good agreement with the value of 3.2(2) kcal/mol deduced recently[15] from microwave intensity measurements, thereby establishing conclusively for the first time the correct value from the wide range[15] obtained by a variety of methods. The asymmetry δ_a in the Stark frequencies was calculated from ρ and δ to be 6.83(24) kHz, which is in agreement with the measured value of 7.8(9) kHz.

Three possible sources of error must be considered. First, the V_6 term in the hindering potential[1,2] has been neglected. If $|V_6/V_3| < 5\%$, the only change[16] in Eq. (1) is that a_1 is multiplied by a correction factor λ. The error limits on s and V_3 were recalculated to allow for $|V_6/V_3| \leq 1\%$, the upper limit that is usually taken.[1] The limits on s increased to 1.2%, but those on V_3 did not change significantly because the hyperfine contribution remains dominant. *However*, Eq. (2) is *not* altered at all because λ cancels along with a_1. Thus the value of ρ obtained is *independent* of V_6. Second, theoretical estimates show the terms[5] arising from torsion-vibration interactions are insignificant. This conclusion is confirmed by the fact that δ and δ_a were observed to independent of J. Third, the σ-dependent terms in μ were shown to be negligible.

At the present level of approximation, the current technique has yielded a value of V_3 that is comparable in accuracy with the best determination made previously in symmetric tops and with typical determinations made in asymmetric rotors.[14] Because of the cancellation of errors, it is possible at this level to study[17] small isotope shifts in V_3 which can be used to examine the contribution of zero-point vibration to the barrier. Furthermore, the method has yielded the first direct determination of I_α for a symmetric top. The fact that I_α is directly available from the data is of considerable importance, because the error in I_α usually determines[2] the error in V_3. If I_α must be obtained from the structure, then the accuracy of V_3 is limited to the order of 1%. This limitation is not faced here. Once the hyperfine corrections have been calculated, the accuracy for both I_α and V_3 should be greatly improved beyond the present level. The method can be applied[7] to other symmetric rotors with internal tops provided $|A_0 - B_0| \lesssim 5$ GHz and $\mu \gtrsim 1$ D.

The present experiment indicates that it should be possible to study internal rotation with distor-

tion-moment microwave spectroscopy[17] in systems where the barrier is much lower and the splittings are much larger. Although many applications of these $\Delta K = \pm 3$ microwave lines have been discussed,[18] this opportunity appears to have been previously overlooked. By studying the high-J states in the microwave and the low-J states with MBER, a great deal can be learned about the potential barrier, the torsion-vibration interaction, and nuclear spin–internal rotation hyperfine effects in systems which are much simpler than asymmetric rotors. Experiments of this type are currently underway. A full report of the current work will be published elsewhere.

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Polarization of a Two-Electron, One-Photon K X-Ray Transition

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We have observed a large linear polarization for the low-energy $K\alpha$ x-ray satellite, KL^1 radiative electron-rearrangement (RER) ($1s^{-1}2p^{-1}{}^1P_1 - 2s^{-2}{}^1S_0$) two-electron, one-photon transition, in Si and Al targets when bombarded by 2.0-MeV He. This observation supports the interpretation of the origin of the KL^nRER satellites since both the $K\alpha'$ polarization and the KL^1RER polarization reflect the nonstatistical population of the magnetic substates of the initial state.

In recent publications[1,2] we have reported observations concerning the radiative decay of single-K-, multiple-L-shell vacancy states of third-period elements following ionization by heavy-ion projectiles. The two observations were that (1) the $1s^{-1}2p^{-1}{}^1P_1$ vacancy configuration can undergo a two-electron, single-photon, radiative electron-rearrangement (RER) transition[3] to a $2s^{-2}$ final configuration giving rise to a low-energy $K\alpha$ satellite x ray; and (2) the magnetic substates of the $1s^{-1}2p^{-1}{}^1P_1$ state are not statistically populated when the $^1P_1$ states are produced by light-ion ($1 \leq Z \leq 3$) bombardment,[4] thereby producing plane-polarized radiation in the subsequent decay $K\alpha'$ ($1s^{-1}2p^{-1}{}^1P_1 \rightarrow 2p^{-2}{}^1S_0$). In this Letter we report an experimental observation of the linear polarization of the two-electron, single-photon decay, KL^1RER ($1s^{-1}2p^{-1}{}^1P_1 \rightarrow 2s^{-2}{}^1S_0$).

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