ble for those strong $M1$ states in the Mg isotopes. It is possible that current effects explain the two discrepancies noted above.

In summary, we have shown that (p, n) cross sections and $B(M1)$ values obtained with electromagnetic interactions are strongly correlated for ^{24,25,26}Mg, as shown in Fig. 3. It appears then that (p, n) reactions at energies above 30 MeV will be a powerful probe for spin-isospin-flip strength in nuclei and may be especially useful in the heavier nuclei.

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Breakdown of the Point-Group Symmetry of Vibration-Rotation States and Optical Observation of Ground-State Octahedral Splittings of $^{32}SF_6$ Using Saturation Spectroscopy

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It is shown that the mixing of vibration-rotation states by nuclear hyperfine interactions causes crossover resonances to appear in infrared saturation spectra. Examples are displayed in the ν_3 band of SF_6 and obtain the tensor centrifugal-distortion constant t_{044} and the tensor spin-rotation constant c_d. The value of t_{044} (5.7 Hz) obtained is in excellent agreement with the theoretical value. A splitting is also demonstrated between vibration-rotation states which differ only in their parity.

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In this Letter we report the first direct experimental observation of the breakdown of the point-group labeling of molecular states through the mixing of vibration-rotation (VR) states of different symmetry species by nuclear hyperfine interactions. This mixing is the basis for a new method in molecular spectroscopy, which applies crossover resonances in saturation spectroscopy to the determination of fine-structure spectroscopic constants. We illustrate this method in the case of the ν_3 band of SF_6 and determine the very small tensor centrifugal-distortion constant t_{044}. In the course of this work we have also made the first determination of the hyperfine tensor spin-rotation constant c_d. We expect this method to have wide applicability to the determination of small spectroscopic constants in molecules.

The origin of this work lies in the observation in the ν_3-band saturation spectrum of SF_6 of many

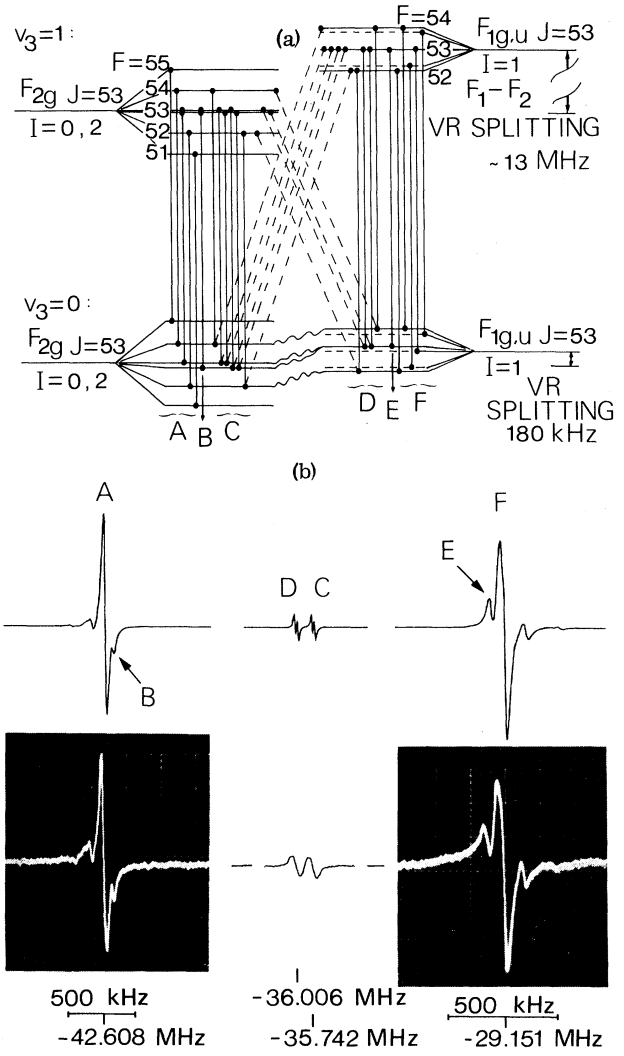

FIG. 1. (a) Energy level diagram for the F_2^6-F_1^6 $Q(53)$ ν_3 lines of SF_6 and associated resonances. Only main resonances and crossovers of interest for the present discussion are presented and labeled A–F here and in (b). Dotted lines indicate F_{1u} levels and wavy lines connect the interacting F_{1g} and F_{2g} levels. (b) Calculated [half width at half maximum (HWHM), 20 kHz] and observed spectra corresponding to (a). The E-F splitting between F_{1u} and F_{1g} resonances is clearly resolved for the $F = 53$ component. Measured detunings are from $Q(45)$ F_2^7.

additional resonances which appear exactly in the center of the interval between main resonances.[1-3] Typical examples are the resonances between the F_1^6 and F_2^6 components of $Q(53)$ that can be seen in Fig. 1 and between the E^0 and F_1^0 components of the $Q(38)$ triplet in Fig. 2. We report a quantitative demonstration that these peaks are crossover resonances between the main $\Delta C = 0$ components (C is the VR-symmetry species defined below) and forbidden $\Delta C \neq 0$ transitions.[4] The normal infrared selection rule $\Delta C = 0$ can be violated if the point-group–symmetry species are mixed, and we shall see that, because of the small value of the centrifugal-distortion constant t_{044} (primarily responsible for the VR splittings in the ground state), hyperfine interactions may substantially mix adjacent VR states even if they have different point-group symmetry. The $\Delta C \neq 0$ lines are usually too weak and too close to $\Delta C = 0$ lines to be observed directly but fortunately in saturation spectroscopy, crossover resonances appear halfway between two resonances that share a common state (if their frequency separation is within the Doppler width) and the crossover intensities are roughly the geometrical means between those of the parent lines.[5] Figure 1 illustrates the case of an F_1-F_2 doublet. The VR splitting in the $\nu_3 = 1$ state (primarily due to the constant $t_{224} \gg t_{044}$) is usually orders of magnitude larger than in the ground vibrational state. In this case the new transitions give rise to two easily distinguishable sets of crossover resonances: (i) Crossovers with common upper states (not represented on the energy diagram of Fig. 1) which appear as satellites of the main lines. (ii) Crossovers with common lower states that are well isolated and are thus easy to observe and analyze without interference from other resonances. Their structure reveals the ground-state VR splittings.

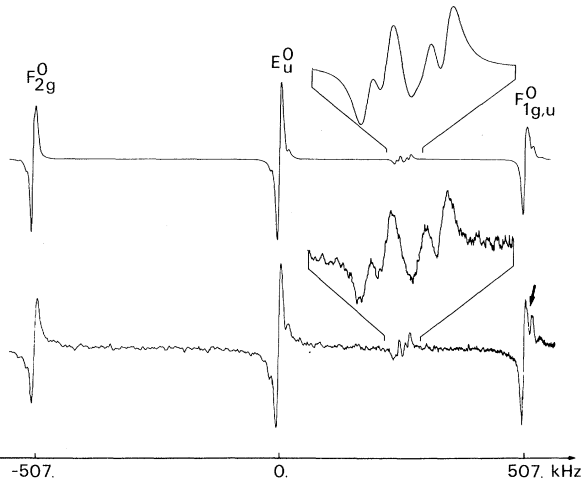

FIG. 2. Calculated (top) and observed (bottom) spectra for the $Q(38)$ $F_2^0E^0, F_1^0$ cluster (HWHM = 5 kHz). The F_{1u} $F = 38$ component is clearly visible on higher-resolution recordings of the F_1 resonance and is indicated here by an arrow.

To give a short summary of the theory, we shall recall that the total wave function Ψ is the tenso-

rial product of a nuclear-spin wave function Ψ_{NS} and of a VR wave function Ψ_{VR}. These wave functions are labeled according to their symmetry species in the group $O(3)\times G$ which is the product of the orthogonal group in the laboratory frame with the point group of the molecule.[6] In the case of octahedral spherical-top molecules ($G \equiv O_h$) such as SF_6, where the spin of the outer nuclei is half-integral, Ψ must be A_{2u} in order to satisfy the Pauli principle:

$$\Psi^{(F_T, A_{2u})} = [\Psi_{VR}^{(J_T, nC)} \times \Psi_{NS}^{(I_g, C')}]^{(F_T, A_{2u})}, \quad (1)$$

where F_τ, J_τ, and I_g specify the representations in O(3); A_{2u}, C, and C' specify the representations in G; and where n distinguishes identical representations for the VR wave functions. The nuclear-spin wave functions have only certain definite symmetry species[7] C' in O_h: A_{1g}, A_{2g}, A_{2u}, E_g, F_{1u}, F_{2u}, and F_{2g}. The consequence of the Pauli principle is therefore that VR states may only be of species[6] $C = A_{1g}$, A_{1u}, A_{2u}, E_u, F_{1u}, F_{1g}, or F_{2g}. In the ground vibrational state, the *ungerade* and *gerade* character in O_h is identical to the overall parity[6] which is conserved by hyperfine interactions (neglecting possible parity-violating weak interaction effects). Thus the crossovers between lines corresponding to ground states of opposite parities will be missing: e.g., the crossover between $E_u{}^0$ and $F_{2g}{}^0$ in Fig. 2. Similarly, the hyperfine operators are tensorial products of a nuclear-spin operator with a VR operator[8-10]:

$$H^{(O_g, A_{1g})} = [H_{VR}^{(k_g, C)} \times H_{NS}^{(k_g, C)}]^{(O_g, A_{1g})}. \quad (2)$$

Only the overall operator must be invariant under the operations of $O(3)\times G$. Each of the two parts may be a tensor ($C \neq A_{1g}$); the possibility of coupling VR states of different symmetry species in G arises from this fact.[11] In the vibronic ground state of octahedral XY_6 molecules, the strongest hyperfine couplings (spin-rotation and spin-spin interaction) lead to $C = A_{1g}$ (spin-rotation), E_g (spin-rotation and spin-spin), and F_{2g} (spin-spin). We have derived the explicit forms of these operators, following the methods applied to T_d molecules by Itano.[9] Their matrix elements were evaluated with use of the Wigner-Eckart theorem for doubly tensorial operators by the methods developed for spherical-top molecules by Michelot, Bobin, and Moret-Bailly.[10] The matrix elements of the VR Hamiltonian were evaluated by standard methods (in $v_3 = 1$ the off-diagonal corrections are included). A detailed account of this theory will be given elsewhere. After diagonalization the spectral profile is reconstructed with use of the theory of intensities in low-field saturation spectroscopy[5] and Lorentzian line shapes. From the comparison with observed crossover structures, we infer the values of the unknown constants t_{044} and c_d. The other constants (scalar spin-rotation constant c_a and spin-spin constants d_1, d_2) were fixed equal to the values given by Ozier, Yi, and Ramsey.[12] Also the spin-vibration interaction that occurs for the excited state[3,13] may be neglected for high-J, Q-branch lines. The following clusters present well-resolved crossover structures and have been studied in some detail with the saturation spectrometer described by Bordé *et al.*[3]: $Q(51)$ $F_{2g}{}^6$, $F_{1g,u}{}^6$; $Q(53)$ $F_{2g}{}^6, F_{1g,u}{}^6$; $Q(54)$ $A_{2u}{}^2, E_u{}^4$; $Q(55)$ $F_{2g}{}^6, F_{1g,u}{}^6$; $Q(38)$ $F_{2g}{}^0, E_u{}^0, F_{1g,u}{}^0$. In $Q(51)$, $Q(54)$, and $Q(55)$ the crossovers appear as doublets as in $Q(53)$ (Fig. 1). We use the splittings of these four doublets as well as the $Q(38)$ quadruplet contour (Fig. 2) to adjust the values of t_{044} and c_d. We obtain

$$t_{044} = 5.7 \pm 0.7 \text{ Hz}, \quad (3)$$

$$|c_d| = 8.5 \pm 2 \text{ kHz}, \quad (4)$$

where the sign of t_{044} is unambiguously determined by the $Q(38)$ case.

The good agreement between observed and calculated spectra can be seen in Fig. 1 for $Q(53)$ and on Fig. 2 for $Q(38)$. With $t_{044} = 5.7$ Hz and $|c_d| = 8.5$ kHz, the calculated (observed) splittings are 210 kHz (235 kHz) in $Q(55)$, 250 kHz (243 kHz) in $Q(54)$, 265 kHz (265 kHz) in $Q(53)$, and 345 kHz (325 kHz) in $Q(51)$. The observed intensities of crossover resonances are usually larger than predicted because a differential saturation occurs between the main peaks and the crossover resonances for the laser powers used to record these spectra. The theoretical intensities would be obtained only in the limit of vanishing laser intensity.

One should point out that the t_{044} given by (3) is a phenomenological parameter and that its value may change when higher-order terms are introduced in the VR Hamiltonian (among other terms our t_{044} includes the effects of $t_{044}{}^{01}$ and t_{066}). The value of 5.7 Hz is in excellent agreement with the value 5.6 ± 0.5 Hz derived from the formula of Berger[14]:

$$t_{044} = B_e{}^3[\omega_5{}^{-2} - \omega_2{}^{-2}]/5, \quad (5)$$

where $B_e \simeq B_0 = 0.09111$ cm^{-1} is the equilibrium rotational constant and where[14] $\omega_5 = 529 \pm 7$ cm^{-1}

and $\omega_2 = 654 \pm 2$ cm^{-1}. This agreement suggests that the previous formula could have a predictive value for other octahedral molecules such as UF_6.

The detailed profiles of the F_1 components of both $Q(38)$ and $Q(53)$ show the splitting of the F_{1g} and F_{1u} lines. The degeneracy of the corresponding levels is lifted by diagonal matrix elements of the tensor hyperfine interactions and by off-diagonal matrix elements involving other VR states.

In conclusion, we have developed a quantitative method for the study of small fine-structure splittings between energy levels in the ground vibrational state of polyatomic molecules based on the analysis of crossover resonances in saturation spectra and have illustrated this method for the spectrum of SF_6. It is important to emphasize the role played by the overall parity of the VR states. Up to now overall parity was often disregarded in infrared molecular spectroscopy, and most recent papers label SF_6 levels in the point-group O and not in O_h. It is necessary for us to introduce the parity to account for the missing crossovers. In addition, we have experimentally demonstrated that because of hyperfine interactions a splitting exists between VR states which differ only in their parity even in the absence of tunneling effects between different equilibrium configurations.

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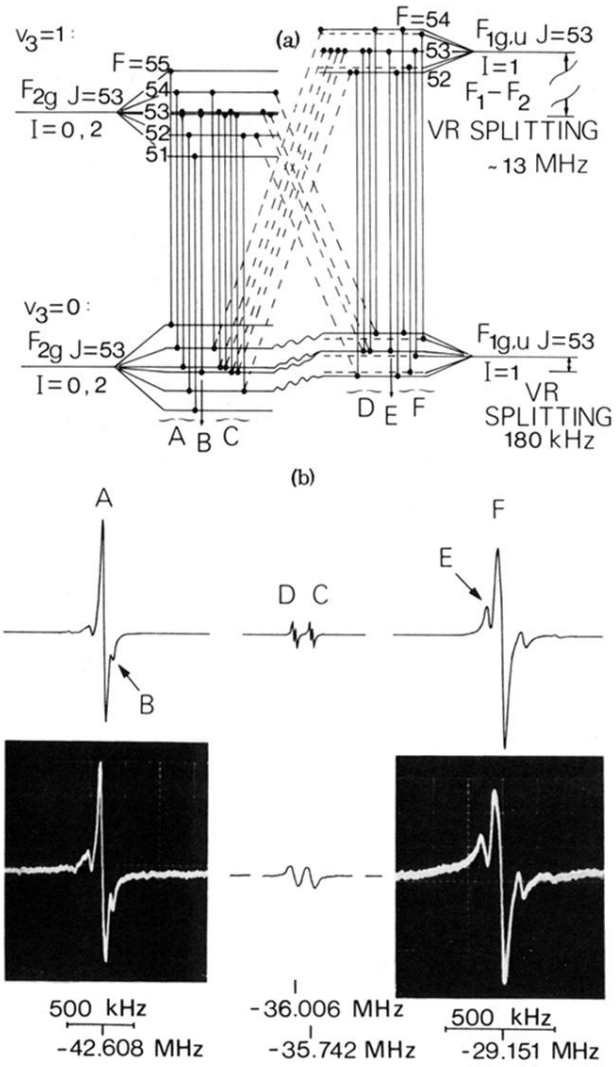

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