

Evidence of tumbling multiplets in saturation absorption spectra of SiF₄

William G. Harter*

Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colorado 80309

Howard P. Layer

Center for Absolute Physical Quantities, National Bureau of Standards, Washington, D.C. 20234

F. R. Petersen

Time and Frequency Division, National Bureau of Standards, Boulder, Colorado 80303

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Some implications of tumbling quartets, triplets, and doublets seen in high-resolution spherical-top spectra are discussed. Some of the first observed cluster splittings are shown in SiF₄ spectra and compared with the predictions of the quantum theory of clusters. Further potentially interesting spectroscopic experiments are proposed.

In this Letter we draw attention to new kinds of spectral features called "clusters." Clusters may appear in any region of a spectrum of heavy spherical-top molecules, or, for that matter, in any spectrum of a symmetric polyatomic molecule. So far they have shown up mostly in infrared spectra of tetrafluorides and hexafluorides. A cluster differs from an ordinary rovibronic fine-structure line in that it contains several tightly clustered lines, and it usually appears to be a single, more-intense line. Closer examination of clusters with devices of higher spectral resolution promises to yield a great deal of information about structure and dynamics of a number of different types of molecules. The first and tentative close looks at clusters are discussed here, along with some of the theoretical and experimental implications of this new kind of spectral object.

A new quantum theory¹⁻³ of spherical-top dynamics predicts the form of spectral clusters that occur in vibrational spectra of molecules having tetrahedral (XY₄), octahedral (XY₆), or cubic (XY₈) structure. The clusters had been noticed earlier in computer calculations of octahedrally invariant model Hamiltonians by Lea *et al.*,⁴ Dorney and Watson,⁵ and Fox *et al.*⁶ Dorney and Watson gave a classical explanation of the unexpected sixfold and eightfold rotational degeneracies by supposing stable rotation around any of the six S₄ symmetry axes or else around any of the eight C₃ symmetry axes. The recently developed quantum theory of clusters¹ tells which symmetry species, A₁, A₂, E, F₁, or F₂, occur within a given cluster and predicts their ordering and relative spacing. The theory supposes that a slow precessional tumbling between symmetry axes is superimposed upon the faster rotation around the axes. The precession or tumbling rate is

quantified by a tunneling parameter *S* whose magnitude varies from cluster to cluster in a predictable way.²

Clusters belonging to threefold axes generally have greater tunneling amplitudes, and their splitting is therefore easier to resolve. The tumbling quartet (A₁ ⊗ T₁ ⊗ T₂ ⊗ A₂) is shown in Ref. 1 to correspond to states of rotational momentum (*n*) evenly divisible by three. This is labeled (0₃), which implies that (*n*) is zero modulo three (*n* = 0 mod 3). The tumbling splitting gives the energy levels

$$\begin{aligned} E^{A_2} &= H + 3S, \\ E^{T_2} &= H + S, \\ E^{T_1} &= H - S, \\ E^{A_1} &= H - 2S, \end{aligned} \quad (1)$$

where *H* is the cluster center of gravity. The other types of threefold clusters labeled (1₃) and (2₃) are both tumbling triplets (T₁ ⊗ E ⊗ T₂) with energy-level splittings predicted in Ref. 1 by

$$\begin{aligned} E^{T_2} &= H + 2S, \\ E^E &= H, \\ E^{T_1} &= H - S. \end{aligned} \quad (2)$$

The fourfold clusters labeled (0₄) and (2₄) [(0₄) = A₁ + T₁ + E and (2₄) = A₂ + T₂ + E] are triplets also. However, (ATE) clusters have a predicted 2:1 tumbling splitting as given by

$$\begin{aligned} E^A &= H + 4S, \\ E^T &= H, \\ E^E &= H - 2S. \end{aligned} \quad (3)$$

Finally, there are fourfold tumbling doublets ($T_1 + T_2$) labeled (1_4) (3_4) . Also, twofold giant clusters exist in certain situations.^{1,7}

While computer model spectra^{5,6} indicate that Eqs. (1)–(3) have the correct form, it is important to see whether real molecular spectra have this form, too. The extremely high resolution of laser saturation-absorption spectra makes it possible to resolve the splittings within many spectral clusters. The first such experiments involving SiF_4 and SF_6 were done by the present coauthors Layer and Peterson and independently by Rabinowitz *et al.*⁸ several years ago. The former experiment used a waveguide CO_2 laser to increase the frequency scan.

In one such scan (Fig. 1) there are two features that appear to be threefold clusters ($A_1 + T_1 + T_2 + A_2$) and ($T_1 + E + T_2$). The forms of their splittings obey Eqs. (1) and (2), respectively, and the spin statistical weights,^{3,9} ($A_1:T_1:T_2:A_2$) = (5:3:3:5) and ($T_1:E:T_2$) = (3:2:3), are close to the ratio of heights within each cluster. A number of similar cluster splittings have been seen in other results of saturation-absorption experiments using CO_2 10- μm radiation.^{10,11} The cluster splittings in SF_6 have the same form; only the statistical weights^{12,13} are different: ($A_1:A_2:E:T_1:T_2$) = (2:10:8:6:6).

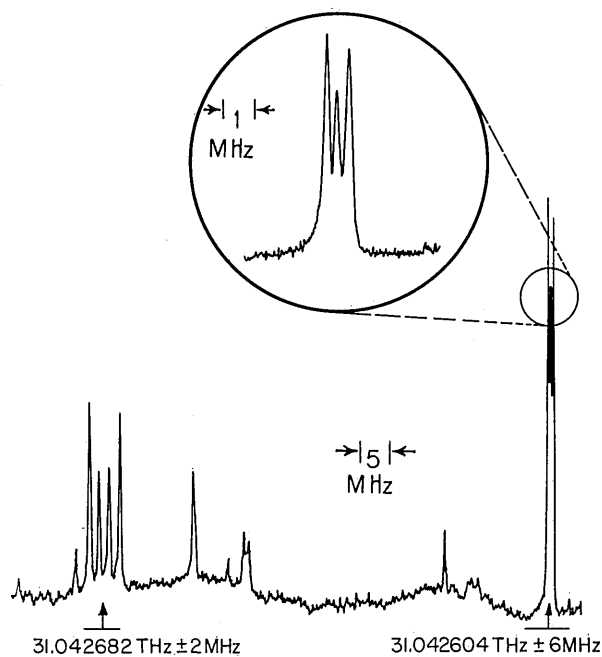


Fig. 1. Saturated absorption spectrum of SiF_4 by waveguide CO_2 laser in vicinity of $P(32)$ line of the 9.4- μm band (31.042718 THz). Absorption cell is 1 m long, with a pressure of 5×10^{-3} Torr. CO_2 laser is 10 cm in length at 150 Torr, with the flow changing 80 times/sec with a $\text{CO}_2:\text{N}_2:\text{He}$ mixture ratio of 13:12:74. Quartet feature on the left-hand side is evidently a threefold cluster (0_3) = ($A_1 + T_1 + T_2 + A_2$). For tetrahedral molecules the statistical weights of A_1 and A_2 are the same and so there is not enough information available yet to tell which comes first. The same is true for the ($T_1 + E + T_2$) cluster on the right-hand side of the figure. Note that the enlarged view in the circle is meant to magnify the frequency scale, but it does not alter the observed intensities of the lines. When clusters are not resolved, their intensities tend to pile up, as shown in the unmagnified line.

Hence all results so far indicate that high-resolution spectra of spherical-top molecules can be identified easily and that the quantum theory of clusters is a useful theory. Since this theory has given simple accurate algebraic formulas¹⁴ for complete bands of cluster line frequencies around 947 cm^{-1} in SF_6 and around 631 cm^{-1} in CF_4 , it should be easy to analyze completely most $\text{XY}_{4,6,8}$ rovibrational spectra. This should lead to a complete and convenient set of frequency standards for the infrared spectrum.

Finally, these results open up possibilities for exploring the physical and chemical implications of the clustering.¹⁵ The cluster tunneling rate or splitting parameter S decreases nearly exponentially with the axial momentum n . [It reaches a value of about 3 mHz in a $P(54)$ cluster of the ν_4 band in CF_4 .] At some point, the hyperfine splitting caused by nuclear spin rotation will dominate the cluster splitting. Beyond this point the gyroscopic action of the nuclear spins will quench the tumbling altogether, and the molecule will be pinned on one of its internal axes. The standard spin species A_1 , A_2 , E , T_1 , and T_2 will be mixed into particular combinations to accommodate the spontaneous symmetry breaking within the molecule, and the hyperfine spectra will take an extraordinary form.

Clearly it is important to examine tighter and tighter clusters with higher and higher resolution in order to study the effects of tumbling and nuclear spins. One could propose that the molecule OsO_4 is a good candidate since one can use oxygen isotopes with or without spin. However, it appears that SiF_4 , SF_6 , SiH_4 , and CD_4 are the only spherical tops that fall within reach of the CO_2 - ($\sim 10\text{-}\mu\text{m}$) laser saturation-absorption devices. Of these, only SiF_4 is a heavy tetrahedral top carrying spin- $1/2$ nuclei. CD_4 carries spin-1 nuclei, which might be interesting later on when more theory is understood, though it may be too light to have good clusters showing at room temperature. Unfortunately, necessary details of SiF_4 spectra are not yet available. One still needs a good set of Fourier-transform and laser-diode spectra to find SiF_4 molecular constants. Then and only then can cluster theory give formulas that tell which clusters have resolvable splittings and where they lie. On the other hand, SF_6 is well assigned, but its hyperfine theory is more complicated and may discourage experimentalists from thinking about it in the immediate future. Nevertheless, the predicted presence of superclusters in SF_6 (Refs. 3,16) and their subsequent observation by Ch. J. Bordé and M. Ouhayoun¹⁷ gives many intriguing possibilities for the theorist.

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* Present address: School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332.

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