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STRONG FIELD STARK EFFECT

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ABSTRACT

The energy levels of a rigid asymmetric rotor containing one or more quadrupolar nuclei and subject to an electric field are discussed for the case in which the Stark effect energies are larger than those arising from quadrupole coupling effects.

The theory is applied to quantitative Stark effect measurements on $COCl_2^{35}$ and $CH_2CCl_2^{35}$. The dipole moments determined by this method are 1.17 and 1.34D, respectively.

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The topic of the energy levels of a rigid rotor containing at least one quadrupolar nucleus and subject to a space fixed electric field has been discussed by a number of authors. Fano[1] has considered the case of a linear rotor; Low and Townes[2] extended the theory to the symmetric rotor; and Mizushima[3] has discussed the asymmetric rotor. However, although the problem is in principle solved, there appears to be no discussion of the explicit results for the asymmetric rotor in the strong field case or of the simplifications in computational and experimental procedure which result in certain cases. These simplifications, and their use, will be discussed below; we shall begin with a brief resume of the theory.

The so called "first order" Hamiltonian, which correctly specifies those matrix elements of the quadrupole energy which are diagonal in J, is given by

$$H_Q = \Sigma_i \, eQ_i \left\langle \left(\frac{\partial^2 V}{\partial z^2}\right)_i \right\rangle \left[3\left(\underset{\sim}{I}_i \cdot \underset{\sim}{J}\right)^2 + \frac{3}{2}\left(\underset{\sim}{I}_i \cdot \underset{\sim}{J}\right) - \underset{\sim}{I}_i^2 \, \underset{\sim}{J}^2 \right]$$

$$\times \left[2J(2J-1)\, I_i\, (2I_i-1) \right]^{-1}$$

The level splitting factor $eQ_i \left\langle \left(\frac{\partial^2 V}{\partial z^2}\right)_i \right\rangle$ may be expressed as

$$eQ_i \left\langle \left(\frac{\partial^2 V}{\partial z^2}\right)_i \right\rangle = \underset{\sim}{\Phi} \, \underset{\sim}{\chi}^{(i)} \, \underset{\sim}{\Phi}$$

where the components of the vector $\underset{\sim}{\Phi}$ are the direction cosine operators relating the space fixed z axis with the molecule fixed abc axes; $\underset{\sim}{\chi}^{(i)}$ is the quadrupole coupling tensor for the ith nucleus and is a molecular constant.

The presence of an electric field E along the z axis gives rise to an additional contribution to the energy specified by $H_E = -E \, \underset{\sim}{\mu} \cdot \underset{\sim}{\Phi}$. The total energy is then the sum of H_Q, H_E, and H_o, the latter being the usual rigid asymmetric rotor expression.

Since we are interested in the case in which the Stark perturbation is much larger than the quadrupole perturbation, we choose to represent H in the (J,τ, M, I_i, M_i) basis, M_i being the quantum number specifying the value of the $\underline{z}$ component of $\underset{\sim}{I}_i$. The matrix elements of H_o in this basis are well known, cf, Townes and Schawlow.[4] The matrix elements of $\underset{\sim}{\Phi}$ have been described[5] and their use in Stark effect calculations has been thoroughly discussed.[6] Values of these elements are also required in calculating the level splitting factors and may be obtained from published tables of line strengths[4] or by direct calculation with the aid of high speed computers. For the present purpose we shall assume these values as given and remark only that all elements of $\underset{\sim}{\Phi}$ are diagonal in M.

Thus, we are left with the expression $F_i = 3(\underset{\sim}{I}_i \cdot \underset{\sim}{J})^2 + \frac{3}{2}(\underset{\sim}{I}_i \cdot \underset{\sim}{J}) - \underset{\sim}{I}_i^2 \underset{\sim}{J}^2$ as the only remaining operator whose matrix elements must be evaluated. These elements have been given by Kellogg, et al.,[7] and the result for the on-diagonal element is

$$< JMI_iM_i|F_i|JMI_iM_i> = \tfrac{1}{2}\left[3M_i^2 - I_i(I_i+1)\right]\left[3M^2 - J(J+1)\right].$$

The only nonvanishing off-diagonal elements satisfy the relations $\Delta M = \pm 1$, $\Delta M_i = \mp 1$ or the relations $\Delta M = \pm 2$, $\Delta M_i = \mp 2$; accordingly there are no off-diagonal terms which simultaneously contain a contribution from H_Q and H_S. Since we are interested in the strong field case, ie, the situation in which the effect of the off-diagonal terms of H_Q is negligible compared to that of the H_S terms, we shall have no need for these values of the elements of H_Q.

APPLICATION

In certain cases the theory of the previous section takes on a particularly simple form. It is the purpose of this section to show how this occurs and to present the experimental results for $CH_2CCl_2^{35}$ and for $COCl_2^{35}$.

In the (J,τ, M, I_i, M_i) basis, and for a rigid asymmetric rotor containing two equivalently situated quadrupolar nuclei of spin 3/2, we have

$$< J\tau M\ 3/2\ M_1\ 3/2\ M_2 | H_Q | J\tau M\ 3/2\ M_1\ 3/2\ M_2 > =$$

$$eQ < \frac{\partial^2 V}{\partial z^2} > [\ 3M^2 - J(J+1)]\ [12J(2J-1)]^{-1} [3M_1^{\,2} + 3M_2^{\,2} - 15/2]$$

where

$$eQ < \frac{\partial^2 V}{\partial z^2} > = \Phi_{za}^2\ \chi_{aa} + \Phi_{zb}^2\ \chi_{bb} + \Phi_{zc}^2\ \chi_{cc}$$

and the nucleus index is no longer required. The M_1 dependent term above can assume the three values +6, 0, and -6. The occurence of the value zero leads to a set of levels l specified by $M_1^{\,2} + M_2^{\,2} = 10/4$ and $-J \leq M < J$ which for zero Stark field are completely degenerate.

Examination of the off-diagonal elements of F^7 shows that various members of this degenerate set will be connected by elements of H_Q. Since application of an electric field will remove the degeneracy between the level M=0 and the other magnetic sublevels, we see that for sufficiently large field these off-diagonal terms in H_Q may be ignored and the (J,τ, M, I_i, M_i) representation becomes appropriate.

These considerations suggest that in the strong field case quantitative Stark effect data for the M=0 component of an R branch transition will be relatively simple to interpret. In addition, it is found experimentally that inhomogeniety of the Stark field leads to broadening of the absorption lines and a consequent decrease in accuracy. Hence, there is the added requirement that this transition is one which is easily "driven" into the strong

field case. This consideration suggests that a $0 \rightarrow 1$ transition would be appropriate: The $J = 0$ level is not perturbed by H_Q and, in the usual case, the energy of $J = 1$ $M = 0$ will increase with increasing E while that of the levels $J = 1$ $M = \pm 1$ will decrease.

Thus, for the two molecules of concern here, attention was confined to the $0_{00} \rightarrow 1_{11}$ transition. For this transition the appearance of the absorption line once the strong field case has been reached will be that of a symmetric triplet with the center member being the most intense. Since there are no near degeneracies amongst the J=0,1,2 levels coupled by H_S the frequency will vary linearly in E^2. Moreover, when a plot of frequency versus E^2 is made the straight lines resulting from the strong field case when extrapolated to $E^2 = 0$, will yield the frequencies ν_0 and $\nu_0 \pm eQ < \frac{\partial^2 V}{\partial z^2} >$, ν_0 being the frequency corresponding to H_0 alone. Since ν_0 can be directly observed, and since $eQ < \frac{\partial^2 V}{\partial z^2} >$ is obtainable from χ, one can use these values as well as the characteristic triplet appearance to prove that the strong field case has been reached.[8] Lastly, it should be noted that since H_Q makes no contribution to the frequency of the center member of the triplet, strong field data for this component may be treated as if quadrupole coupling were absent.

Subject to experimental limitations the predictions above were confirmed for both $COCl_2{}^{35}$ and $CH_2CCl_2{}^{35}$. The results obtained for $COCl_2{}^{35}$ are shown in Fig. 1 which is a plot of the observed frequency of the center component versus E^2. The solid line shows the strong field observations while the dotted line shows the required extrapolation to the observed ν_0. The strong field triplet was observed but no quantitative measurements could be made on the outer members because of interference by absorption lines with slow Stark effect; at higher fields broadening limited resolution sufficiently so that

only data on the center of the symmetric multiplet could be safely used. Using the rotational constants of Robinson[9] and machine calculated values of the direction cosine elements the data of Fig. 1 yield $\mu = 1.17 \pm .01D$ for $COCl_2^{35}$. A previous measurement by the dielectric constant method gave a value 1.18.[10]

Measurements of the type above were also performed on the $0_{00} \rightarrow 1_{11}$ transition of $CH_2CCl_2^{35}$ and again confirmed the expectations for the strong field case. By an identical procedure and with the rotational constants of Sekino and Nishikawa[11] the value $\mu = 1.34 \pm .01D$ was determined. In this case it proved possible to obtain a measurement of the entire triplet for a field strength of 3.16 esu/cm. For this field, and for the value $\mu = 1.34D$, the calculated frequency interval[12] between the center and the outer components is $\pm$ 1.5 Mc; observed values were -1.3 and + 1.4 Mc.

Lastly, it may be noted that it has not proved possible to make strong field measurements on the $0_{00} \rightarrow 1_{11}$ transition of cis $CHCl^{35}$ $CHCl^{35}$. This fact is in accord with the theory and has its origin in a 0.3 kMc near degeneracy between the 1_{11} and 2_{02} levels. The result is that the energy of both the M=0 and M=1 states of the 1_{11} level decrease with increasing field. Thus, even though Stark displacements in excess of 100 Mc are easily obtained, the M degeneracy is not sufficiently removed to overcome the quadrupole coupling effect.

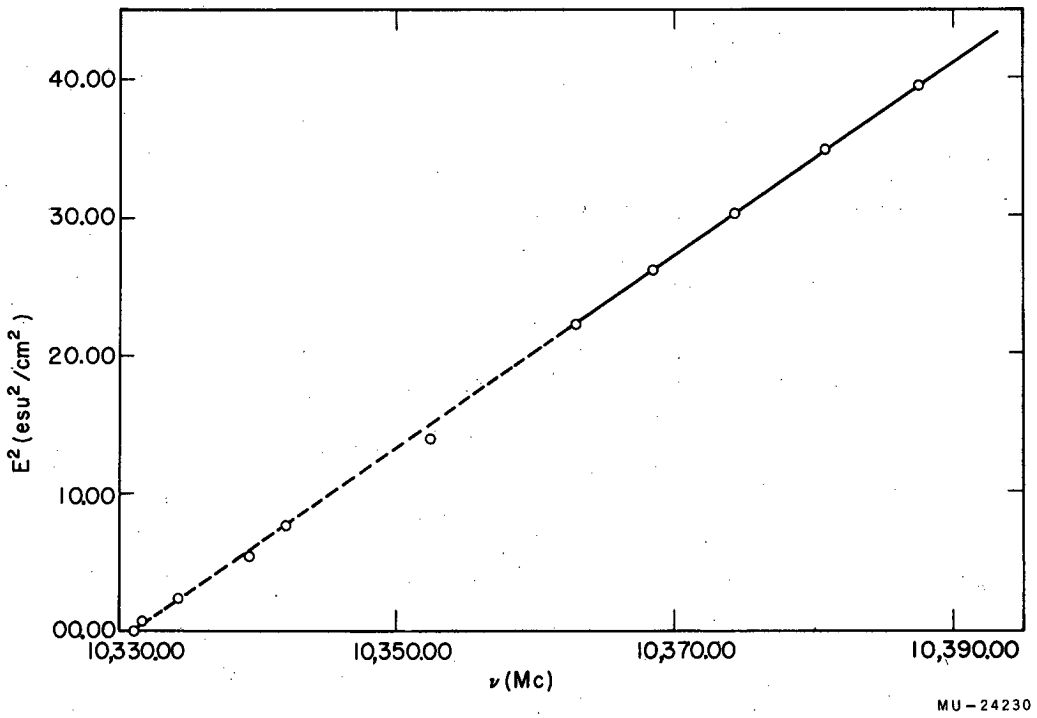
40.00
30.00
20.00
10.00
00.00
E^2 (esu^2/cm^2)
10,330.00
10,350.00
10,370.00
10,390.00
ν (Mc)
MU-24230

Fig. 1

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