4°. The estimated contribution of these two sources of error, (a) and (b) above, is indicated by error bars on the experimental points in Figs. 6–11.

The remaining deviation of the experimental points from the theoretical curves in Figs. 6–11 is thought to be due to the lack of generation of well-defined longitudinal and transverse sound-wave modes throughout the volume of the sample due to unfavorable geometry.[20] In situations where the ratio of sample diameter to sound wavelength is relatively small ($D/\lambda$ was about 7 for longitudinal waves and 17 for transverse waves in the $KTaO_3$ sample) it is found that, if one is trying to generate pure longitudinal waves along the axis of the sample, there is a considerable amount of radial motion perpendicular to the propagation axis in addition to the desired axial motion. In the case of transverse waves it is the polarization axis of the wave that varies in direction as you move over a cross section of the sample which is perpendicular to the propagation direction of the wave. Since in the derivation of Eqs. (2) it was assumed that only pure longitudinal or transverse waves were present, this acoustic-mode conversion can be expected to cause deviations of the experimental results from theory.

It is believed, however, that the agreement shown in Figs. 6–11 is sufficiently good that the nature of the coupling between the acoustic phonons and the nuclear spins in $KTaO_3$ is understood and, in fact, occurs through the quadrupolar interaction.

## ACKNOWLEDGMENTS

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# Zeeman Splitting of Vibronic Levels for Octahedral Actinide and Lanthanide Complexes, Free and in Crystals*

R. A. SATTEN, D. R. JOHNSTON, AND E. Y. WONG
*Department of Physics, University of California, Los Angeles, California*

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The splitting of vibronic levels in the presence of a magnetic field is determined in terms of a few parameters for an octahedral complex in the limit of Zeeman interaction (A) small compared to vibronic splitting, (B) comparable to vibronic interaction, and (C) large compared to vibronic interaction. The relative density of phonon states controls the size of the vibronic splitting in crystals, and is influential in determining whether case A, B, or C above applies. Data for cubic $Cs_2UBr_6$ show that vibronic levels are split according to the parent electronic level, illustrating case C, because the vibronic splitting is much smaller than that which would have occurred for a local-mode or free-ion complex. The free $UBr_6^{2-}$ belongs to case A; the reduction to case C is due to the effect of the phonon relative density of states. The vibronic Zeeman effect is thus a tool for learning about the relative density of phonon states, particularly in localized modes. Similar conclusions apply to vibronic shifts, so that for nonlocalized phonons the vibronic spectra should reflect the density of states of the phonons without the necessity of correction for vibronic shifts or splittings. For case A, particularly applicable to the free-ion complex, the Zeeman splitting of a vibronic level is isotropic and consists of three equally spaced levels with a $g$ value that is one-half that of the parent electronic state. Some general relations between vibronic level differences are derived which are independent of particular models and values of matrix elements.

## I. INTRODUCTION

BECAUSE the octahedral complexes $UCl_6^{2-}$ and $UBr_6^{2-}$ in crystals have tighter binding within the complex than between the complex and neighboring ions, the vibronic spectrum of these ions in crystals shows that they behave in some respects as molecules (i.e., with somewhat localized motion), in that with low resolution, or at not too low a temperature even at high resolution, there are broad bands (about 30-cm$^{-1}$ width) which correspond to excitation or de-excitation of one quantum of an odd (*ungerade*) mode of the complex.[1–3] These bands obey the single-complex-ion vibronic selection rules in that $\Gamma_{4u}$ modes are essentially absent for vibronic transitions between the ground $\Gamma_{1g}$ and excited $\Gamma_{2g}$ electronic states, and $\Gamma_{5u}$ modes are essentially absent for vibronic transitions to excited $\Gamma_{1g}$ electronic states. In addition to the two internal $\Gamma_{4u}$ modes of the molecular ion, a third $\Gamma_{4u}$ band appears at lower energy corresponding roughly to the vibration of the complex

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[1] R. A. Satten, D. J. Young, and D. M. Gruen, J. Chem. Phys. **33**, 1140 (1960).

[2] S. A. Pollack and R. A. Satten, J. Chem. Phys. **36**, 804 (1962).

[3] R. A. Satten, C. L. Schreiber, and E. Y. Wong, J. Chem. Phys. **42**, 162 (1965).

TABLE I. Zeeman effect of vibronic lines and corresponding pure electronic transitions (where known) for trigonal $Cs_2UCl_6$ and cubic $Cs_2UBr_6$ in a field of $27.0\times10^3$ and $25.6\times10^3$ G, respectively. The zero-phonon lines are denoted by (e). Lines are measured to $\pm0.2$ cm$^{-1}$.

| Electronic state | $Cs_2UCl_6$ $\nu$ (cm$^{-1}$) | Pol. | $g$ |
|---|---|---|---|
| $\Gamma_5$ | 21 872.7 | $\pi$ | 0.6 |
| | 21 871.3 | $\pi$ | |
| | 21 866.0 | $\pi$ | 0.6 |
| | 21 864.6 | $\pi$ | |
| | 21 865.2 | $\sigma$ | 0.5 |
| | 21 864.0 | $\sigma$ | |
| | 21 861.0 | $\pi$ | 0.6 |
| | 21 859.5 | $\pi$ | |
| | 21 860.6 | $\sigma$ | 0.5 |
| | 21 859.3 | $\sigma$ | |
| | 21 855.9 | $\sigma$ | 0.6 |
| | 21 854.5 | $\sigma$ | |
| (e) | 21 818.8 | $\sigma$ | 0.7 |
| | 21 817.2 | $\sigma$ | |
| $\Gamma_4$ or $\Gamma_5$ | 20 729.1 | $\pi$ | 1.2 |
| | 20 726.2 | $\pi$ | |
| | 20 533.0 | $\pi$ | 1.3 |
| | 20 530.0 | $\pi$ | |
| | 20 512.0 | $\pi$ | 1.1 |
| | 20 509.4 | $\pi$ | |
| | 20 511.8 | $\sigma$ | 1.1 |
| | 20 509.2 | $\sigma$ | |
| | 20 507.3 | $\sigma$ | 1.2 |
| | 20 504.5 | $\sigma$ | |
| $\Gamma_4$ | 18 875.0 | $\pi$ | 1.2 |
| | 18 872.1 | $\pi$ | |
| (e) | 18 834.1 | $\pi$ | 1.3 |
| | 18 831.1 | $\pi$ | |

| Electronic state | $Cs_2UB_6$ $\nu$ (cm$^{-1}$) | $g$ |
|---|---|---|
| $^3\Gamma_4$ | 18 306.0 | 1.0 |
| | 18 304.7 | 1.3 |
| | 18 303.0 | |
| (e) | 18 259.7 | 1.2 |
| | 18 258.2 | 1.2 |
| | 18 256.7 | |
| $\Gamma_5$ | 17 110.5 | 1.9 |
| | 17 108.1 | 1.9 |
| | 17 105.7 | |
| | 17 000.5 | 1.9 |
| | 16 998.1 | 2.0 |
| | 16 995.6 | |
| | 16 985.1 | 2.0 |
| | 16 982.6 | 2.1 |
| | 16 980.0 | |
| | 16 970.9 | 2.0 |
| | 16 968.4 | 2.1 |
| | 16 965.7 | |
| | 16 961.1 | 1.7 |
| | 16 958.9 | 2.0 |
| | 16 956.4 | |
| $\Gamma_5$ | 15 430.8 | 0.8 |
| | 15 429.8 | 0.9 |
| | 15 428.7 | |
| | 15 427.7 | 0.8 |
| | 15 426.7 | 0.9 |
| | 15 425.6 | |
| $\Gamma_5$ | 12 660.7 | 1.1 |
| | 12 659.3 | 1.2 |
| | 12 657.8[a] | 1.3 |
| | 12 656.2 | 1.1 |
| | 12 654.8 | |
| $\Gamma_5$ | 9 066.5 | 1.0 |
| | 9 065.3 | 0.8 |
| | 9 064.3 | |
| | 9 063.1 | 0.8 |
| | 9 062.1 | 0.9 |
| | 9 061.0 | |

[a] Two lines coincide.

against the positive ions. The three $\Gamma_{4u}$ bands also appear in the far infrared,[4,5] whereas the $\Gamma_{5u}$ internal vibration does not appear, which is in agreement with $k=0$ infrared selection rules.

At high resolution and low temperature, thin crystals of $Cs_2UCl_6$, $Cs_2UBr_6$, and other crystals having $UCl_6^{2-}$ or $UBr_6^{2-}$ complexes show a fine structure[2,6] in the "internal" vibronic bands as well as the low-lying band. It has already been noted[2] that the fine structure cannot be explained on the basis of a single-complex-ion model, nor can the region around one point in the Brillouin zone such as $k=0$ provide enough structure, as often 10 to 20 lines appear within the 20–40 cm$^{-1}$ wide bands.[4,6] In fact, vibronic selection rules[6,7] in the trigonal crystal $Cs_2UCl_6$ show vibronic lines in which

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[4] R. A. Satten and O. M. Stafsudd, *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience Publishers, Inc., New York, 1967), p. 423.

[5] O. M. Stafsudd, Ph.D. dissertation, UCLA, 1967 (unpublished); also available as AEC Research and Development Report UCLA-34P103-3, from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Dept. of Commerce, Springfield, Va.

[6] D. R. Johnston, Ph.D. dissertation, UCLA, 1967 (unpublished).

[7] R. A. Satten, J. Chem. Phys. **40**, 1200 (1964).

TABLE II. Functions used, classified according to irreducible representation and row for the group 0. Normal coordinates in vibronic eigenfunctions stand for the corresponding vibrational eigenfunctions with one quantum of excitation, all other modes being assumed in the $n=0$ vibrational state.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\Gamma_1$: | $V_{ev}$ | $U$ | $P$ | $P'$ | $p'$ | $Q_1^2+2Q_2Q_3$ | $q_1^2-2q_2q_3$ | $q_1q_4-q_3q_5-q_2q_6$ | $(3)^{-1/2}(\psi_1Q_1+\psi_2Q_3+\psi_3Q_2)$ |
| $\Gamma_2$: | $(3)^{-1/2}(\phi_1Q_1+\phi_2Q_2-\phi_3Q_3)$ | | | | | | | | |
| $\Gamma_3$ $\rho=1$: | $(2)^{-1/2}(Y_{22}+Y_{2-2})$ | $V_1$ | $S_1$ | $S_1'$ | $s_1$ | $\frac{1}{2}(Q_2^2+Q_3^2)$ | $\frac{1}{2}(q_2^2+q_3^2)$ | $q_2q_5+q_3q_6$ | |
| $\rho=2$: | $Y_{20}$ | $V_2$ | $S_2$ | $S_2'$ | $s_2$ | $(3)^{-1/2}(Q_1^2-Q_2Q_3)$ | $(3)^{-1/2}(q_1^2+q_2q_3)$ | $(3)^{-1/2}(2q_1q_4+q_2q_6+q_3q_5)$ | |
| $\rho=1$: | $(2)^{-1/2}(\psi_2Q_2+\psi_3Q_3)$ | $(6)^{-1/2}(2\phi_1Q_1-\phi_2Q_2+\phi_3Q_3)$ | | | | | | | |
| $\rho=2$: | $(6)^{-1/2}(2\psi_1Q_1-\psi_2Q_3-\psi_3Q_2)$ | $(2)^{-1/2}(\phi_2Q_3-\phi_3Q_2)$ | | | | | | | |
| $\Gamma_4$ $\rho=1$: | $Y_{10}$ | $f_1$ | $q_1$ | $q_4$ | $\phi_1$ | $(2)^{-1/2}(\psi_3Q_2-\psi_2Q_3)$ | $(2)^{-1/2}(\phi_3q_2-\phi_2q_3)$ | $(2)^{-1/2}(\phi_2Q_3+\phi_3Q_2)$ | |
| $\rho=2$: | $Y_{11}$ | $f_2$ | $q_2$ | $q_5$ | $\phi_2$ | $(2)^{-1/2}(\psi_1Q_3-\psi_3Q_1)$ | $(2)^{-1/2}(\phi_1q_2-\phi_2q_1)$ | $(2)^{-1/2}(\phi_3Q_1-\phi_1Q_2)$ | |
| $\rho=3$: | $Y_{1-1}$ | $f_3$ | $q_3$ | $q_6$ | $\phi_3$ | $(2)^{-1/2}(\psi_1Q_2-\psi_2Q_1)$ | $(2)^{-1/2}(\phi_3q_1-\phi_1q_3)$ | $-(2)^{-1/2}(\phi_1Q_3+\phi_2Q_1)$ | |
| $\Gamma_5$ $\rho=1$: | $(2)^{-1/2}(Y_{22}-Y_{2-2})$ | $W_1$ | $T_1$ | $T_1'$ | $t_1$ | $Q_1$ | $\psi_1$ | $\frac{1}{2}(Q_2^2-Q_3^2)$ | $\frac{1}{2}(q_2^2-q_3^2)$ |
| $\rho=2$: | $Y_{21}$ | $W_2$ | $T_2$ | $T_2'$ | $t_2$ | $Q_2$ | $\psi_2$ | $-Q_1Q_3$ | $q_1q_2$ |
| $\rho=3$: | $Y_{2-1}$ | $W_3$ | $T_3$ | $T_3'$ | $t_3$ | $Q_3$ | $\psi_3$ | $Q_1Q_2$ | $q_1q_3$ |
| $\rho=1$: | $(2)^{-1/2}(\psi_2Q_2-\psi_3Q_3)$ | $(2)^{-1/2}(\phi_2q_2-\phi_3q_3)$ | $-(2)^{-1/2}(\phi_3Q_3+\phi_2Q_2)$ | | | | | | |
| $\rho=2$: | $-(2)^{-1/2}(\psi_1Q_3+\psi_3Q_1)$ | $(2)^{-1/2}(\phi_1q_2+\phi_2q_1)$ | $(2)^{-1/2}(\phi_3Q_1+\phi_1Q_2)$ | | | | | | |
| $\rho=3$: | $(2)^{-1/2}(\psi_1Q_2+\psi_2Q_1)$ | $(2)^{-1/2}(\phi_1q_3+\phi_3q_1)$ | $(2)^{-1/2}(\phi_2Q_1-\phi_1Q_3)$ | | | | | | |

the contributing phonons can be identified as coming, for example, from the $k_z$ axis or the vertical edge of the hexagonal Brillouin zone[4,6] as well as from other regions in other examples.

Although the vibronic Zeeman effect is useful in assigning phonons to regions of the Brillouin zone by use of selection rules,[6–9] our attention is here directed to the splitting of vibronic lines in a magnetic field.

## II. EXPERIMENTAL RESULTS

The essential experimental fact is that within experimental error vibronic levels belonging to the same electronic level have the same splitting in all cases observed, and this is the same as the electronic level splitting when the latter is observable. The data come from $Cs_2UCl_6$ and $Cs_2UBr_6$. Similar results have been obtained for rare earths in anhydrous trichlorides.[8] The results are shown in Table I for a magnetic field of $25.6\times10^3$ G for $Cs_2UBr_6$ and $27.0\times10^3$ G for $Cs_2UCl_6$. Most of the vibronic levels in Table I are from the low-lying optical branches involving largely the motion of the complex against the positive ions. The absence of much Zeeman data on the optical branches which reflect mostly the "internal" modes of the complex is due to the crowded nature of the fine structure in these bands and the difficulty of resolving Zeeman lines under such crowded conditions.

In the next sections we consider theoretically the splitting of vibronic levels under a variety of conditions.

## III. FREE-ION VIBRONIC SPLITTING IN ZERO MAGNETIC FIELD

Since the unperturbed systems are the vibrations of the $XY_6$ molecule in the harmonic approximation and the central ion in the ligand or crystalline field $V_c$ at equilibrium positions, the perturbing vibronic Hamiltonian $V_{ev}$ arises from the difference between the crystalline field at general positions of the atoms and at equilibrium.[10,11] Thus $V_{ev}=\Delta V_c$ is expanded in powers of the displacements of the atoms from equilibrium, which in turn can be expressed in terms of normal coordinates.

We are concerned with vibronic levels involving one quantum of an odd vibration since they permit electric dipole vibronic transitions within the $f^n$ configuration. For this reason, in considering vibronic splittings we need only keep terms of second degree in the normal coordinates. The terms which can appear have a form allowed by symmetry. For the free ion the vibronic Hamiltonian can be divided into a sum of terms involving $\Gamma_{5u}$ modes and $\Gamma_{4u}$ modes which can be considered

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[8] E. Cohen and H. W. Moos, Phys. Rev. **161**, 258 (1967); **161**, 268 (1967).

[9] D. R. Johnston, R. A. Satten, and E. Y. Wong, *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience Publishers, Inc., New York, 1967), p. 429.

[10] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

[11] R. A. Satten, J. Chem. Phys. **29**, 658 (1958); **30**, 590 (1959).

separately. Since there is only one threefold degenerate $\Gamma_{5u}$ vibration, the Hamiltonian is the simplest in this case. It has the form

$$V_{ev}=U(Q_1^2+2Q_2Q_3)+\tfrac{1}{2}[V_1(Q_2^2+Q_3^2)] +V_2(Q_1^2-Q_2Q_3)/(3)^{1/2} +\tfrac{1}{2}[W_1(Q_3^2-Q_2^2)]-W_2Q_2Q_1+W_3Q_1Q_3, \quad (1)$$

where $U$, $V_1$, $V_2$, $W_1$, $W_2$, $W_3$ are functions of $f$ electron coordinates of the central ion which transforms according to the particular row and representation defined in Table II. A word of explanation is in order concerning our choice of normal coordinates $Q_1$, $Q_2$, $Q_3$, which transform according to $\zeta$, $(-\xi+i\eta)(2)^{-1/2}$, $(-\xi-i\eta)(2)^{-1/2}$, respectively, where $\xi$, $\eta$, $\zeta$ in turn transform like $yz$, $xz$, $xy$, respectively. The reason for our choice instead of normal coordinates transforming as $\xi$, $\eta$, $\zeta$ is that atomic wave functions are usually expressed in terms of a $JM$ basis or linear combination of these states in an octahedral field. In particular, we have obtained[3] numerous electronic wave functions generated by simultaneous diagonalization of the Coulomb interaction between $f$ electrons, spin-orbit, and 4th and 6th degree octahedral potential. The electronic basis functions, therefore, already define the particular irreducible representations. There are independent advantages to these particular bases as each row also turns out to span $C_{4h}$ irreducible representations and hence are appropriate when the magnetic field is along one of the fourfold axes. With regard to the electronic parts of $V_{ev}$, $U$, $V_i$, $W_i$, particular expressions can be worked out for special models, such as the point-charge model, but there is value in obtaining results which are independent of special models.

The interesting electronic states are the threefold degenerate $\Gamma_{4g}$ or $\Gamma_{5g}$ since there is no first-order Zeeman effect in $\Gamma_3$ states. The electron-vibration interaction $V_{ev}$ splits the ninefold degenerate vibronic level into four levels according to one of the following direct product decompositions: $\Gamma_{4g}\times\Gamma_{5u}=\Gamma_{2u}+\Gamma_{3u}+\Gamma_{4u}+\Gamma_{5u}$ or $\Gamma_{5g}\times\Gamma_{5u}=\Gamma_{1u}+\Gamma_{3u}+\Gamma_{4u}+\Gamma_{5u}$. For $\Gamma_{1g}$ ground electronic states, as in $UCl_6^{2-}$ and $UBr_6^{2-}$ complexes, the splitting leads to no further structure in the spectrum since only transitions to the $\Gamma_{4u}$ vibronic state are allowed.[2]

Using the vibronic eigenfunctions in Table II, we obtain the following result for the first-order vibronic corrections to the energy of a $\Gamma_4$ electronic state with one quantum of $\Gamma_{5u}$ vibration:

$$E(\Gamma_2)=(5\hbar/2\omega)(\phi_1\mid U\mid\phi_1) -2(3)^{-1/2}(\hbar/\omega)(\phi_2\mid V_2\mid\phi_2) -(\hbar/\omega)(\phi_3\mid W_1\mid\phi_2), \quad (2a)$$

$$E(\Gamma_3)=\tfrac{5}{2}(\hbar/\omega)(\phi_1\mid U\mid\phi_1)-2(3)^{-1/2}(\hbar/\omega)(\phi_2\mid V_2\mid\phi_2) +(\hbar/2\omega)(\phi_3\mid W_1\mid\phi_2), \quad (2b)$$

$$E(\Gamma_4)=\tfrac{5}{2}(\hbar/\omega)(\phi_1\mid U\mid\phi_1)+(3)^{-1/2}(\hbar/\omega)(\phi_2\mid V_2\mid\phi_2) -(\hbar/2\omega)(\phi_3\mid W_1\mid\phi_2), \quad (2c)$$

$$E(\Gamma_5)=\tfrac{5}{2}(\hbar/\omega)(\phi_1\mid U\mid\phi_1)+(3)^{-1/2}(\hbar/\omega)(\phi_2\mid V_2\mid\phi_2) +(\hbar/2\omega)(\phi_3\mid W_1\mid\phi_2). \quad (2d)$$

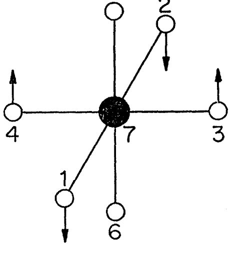

FIG. 1. Atomic displacements corresponding to the normal coordinate $Q_1$ of the $\Gamma_{5u}$ mode of the $XY_6$ molecule.

Note that since $U$ belongs to $\Gamma_{1g}$ the terms involving $U$ produce only a uniform shift in all levels and the three independent energy separations are determined by two independent matrix elements. Thus we obtain a relation between the level separations which is independent of the detailed nature of the interaction. It follows from Eqs. (2) that

$$E(\Gamma_5)-E(\Gamma_4)=\tfrac{2}{3}[E(\Gamma_3)-E(\Gamma_2)] =(\hbar/\omega)(\phi_3\mid W_1\mid\phi_2). \quad (3)$$

The sum of the energy levels (2), each weighted by its degeneracy, equals $(45/2)(\hbar/\omega)(\phi_1\mid U\mid\phi_1)$, a fact which one can also readily predict from the fact that the diagonal sum of the matrix of $V_{ev}$, in a nine-dimensional basis of simple product states of vibrational and electronic wave functions, totals this amount.

The electronic matrix elements in (2) can be replaced by others, as given in the Appendix. Results for a $\Gamma_5$ electronic state are obtainable from (2) and (3) by the following correspondence:

$$\phi_i\leftrightarrow\psi_i, \qquad \Gamma_4\leftrightarrow\Gamma_5,$$
$$\Gamma_5\leftrightarrow\Gamma_4, \qquad \Gamma_3\leftrightarrow\Gamma_3, \qquad \Gamma_2\leftrightarrow\Gamma_1. \quad (4)$$

The energy-level corrections (2) introduced by $V_{ev}$ for $\Gamma_{5u}$ modes all have an implicit mass dependence of $1/M$ since in transforming $V_{ev}$ expressed in terms of displacements of the atoms (halides in our example) to normal coordinates, using mass-weighted coordinates as an intermediate step, one obtains for a typical $\Gamma_{5u}$ mode, as shown in Fig. 1:

$$\Delta Z_1=-\tfrac{1}{2}(M^{-1/2})Q_1, \qquad \Delta Z_2=-\tfrac{1}{2}(M^{-1/2})Q_1,$$
$$\Delta Z_3=\tfrac{1}{2}(M^{-1/2})Q_1, \qquad \Delta Z_4=\tfrac{1}{2}(M^{-1/2})Q_1, \quad (5)$$

where the subscripts label the atoms as shown in Fig. 1 and $M$ is the mass of the halide atom.

We estimate the order of magnitude of the vibronic splitting in a free ion to be of the order of $V_{ev}\simeq V_c(\Delta R/r)^2$, where $\Delta R$ is of the order of a vibration amplitude and $r$ is the $5f$ radius. For $UCl_6^{2-}$ we have[3] $V_c \simeq 10^3$ cm$^{-1}$ and $(\Delta R/r)^2 \simeq 3\times 10^{-3}$, where we have used $\Gamma_5$ modes to estimate $(\Delta R)^2 \simeq \hbar/8M\omega$ and Lenander's[12] value for $\langle r^2\rangle = 47\times 10^{-18}$ cm$^2$. Thus $V_{ev}\simeq 3$ cm$^{-1}$; it depends in any actual case, of course, on the particular electronic level and mode.

There are two sets of $\Gamma_{4u}$ modes of the $XY_6$ molecule, which adds more terms to the Hamiltonian and leads to the diagonalization of a $2\times 2$ matrix to obtain the vibronic eigenvalues.

Suppose $q_1$, $q_2$, $q_3$ are one set of degenerate $\Gamma_{4u}$ modes of frequency $\omega$ and $q_4$, $q_5$, $q_6$ are a second set of frequency $\omega'$, where the bases each transform as spherical harmonics $Y_{10}$, $Y_{11}$, $Y_{1-1}$, respectively. The Hamiltonian has the form

$$\begin{aligned} V_{ev} = {} & P(q_1^2-2q_2q_3)+\tfrac{1}{2}S_1(q_3^2+q_2^2)+S_2(q_1^2+q_2q_3)(3)^{-1/2} \\ & +\tfrac{1}{2}T_1(q_2^2-q_3^2)+T_2q_1q_3+T_3q_1q_2 \\ & +P'(q_4^2-2q_5q_6)+\tfrac{1}{2}S_1'(q_6^2+q_5^2) \\ & +(3)^{-1/2}S_2'(q_4^2+q_5q_6) \\ & +\tfrac{1}{2}T_1'(q_5^2-q_6^2)+T_2'q_4q_6+T_3'q_4q_5 \\ & +p(q_1q_4-q_2q_6-q_3q_5)+s_1(q_2q_5+q_3q_6) \\ & +(3)^{-1/2}s_2(2q_1q_4+q_2q_6+q_3q_5) \\ & +t_1(q_2q_5-q_3q_6)+t_2(q_3q_4+q_1q_6)+t_3(q_1q_5+q_2q_4) \\ & +f_1(q_2q_6-q_3q_5)-f_2(q_1q_6-q_3q_4)-f_3(q_2q_4-q_1q_5), \end{aligned} \tag{6}$$

where the coefficients of the $q$'s are functions of the central ion electrons ($5f$ for $U^{4+}$) and transform as defined in Table II. The terms in $f_i$ do not affect the vibronic energies in first order for either $\Gamma_4$ or $\Gamma_5$ electronic states, since the symmetric products $[\Gamma_4]^2$ and $[\Gamma_5]^2$ do not contain $\Gamma_4$. The $f_i$ affect the energies in second and higher order and are important only if there are close-lying electronic states.

The resulting $2\times 2$ matrices are as follows. The diagonal matrix elements for $\Gamma_5$ electronic states appear as in (2), with the exception that $\psi_i$ must replace $\phi_i$ and $U$, $V_i$, $W_i$ are replaced by $P$, $S_i$, $T_i$, respectively, in $(V_{ev})_{11}$ and by $P'$, $S_i'$, $T_i'$, in $(V_{ev})_{22}$. For $\Gamma_4$ electronic states the resulting expressions just obtained must be changed by the correspondence (4). The off-diagonal elements $(V_{ev})_{12}=(V_{ev})_{21}$ are as follows for $\Gamma_4$ electronic states:

$$\begin{aligned} \Gamma_1\text{:}\quad & [\tfrac{1}{2}(\phi_1|p|\phi_1)-2(3)^{-1/2}(\phi_2|s_2|\phi_2) \\ & -(\phi_3|t_1|\phi_2)]\hbar(\omega\omega')^{-1/2}, \end{aligned} \tag{7a}$$

$$\begin{aligned} \Gamma_3\text{:}\quad & [\tfrac{1}{2}(\phi_1|p|\phi_1)-2(3)^{-1/2}(\phi_2|s_2|\phi_2) \\ & +\tfrac{1}{2}(\phi_3|t_1|\phi_2)]\hbar(\omega\omega')^{-1/2}, \end{aligned} \tag{7b}$$

$$\begin{aligned} \Gamma_4\text{:}\quad & [\tfrac{1}{2}(\phi_1|p|\phi_1)+(3)^{-1/2}(\phi_2|s_2|\phi_2) \\ & +\tfrac{1}{2}(\phi_3|t_1|\phi_2)]\hbar(\omega\omega')^{-1/2}, \end{aligned} \tag{7c}$$

$$\begin{aligned} \Gamma_5\text{:}\quad & [\tfrac{1}{2}(\phi_1|p|\phi_1)+(3)^{-1/2}(\phi_2|s_2|\phi_2) \\ & -\tfrac{1}{2}(\phi_3|t_1|\phi_2)]\hbar(\omega\omega')^{-1/2}. \end{aligned} \tag{7d}$$

For $\Gamma_5$ electronic states one makes the changes given in (4).

It can be shown that relations between vibronic level separations, which are independent of the details of the vibronic interaction, also arise in the coupling with $\Gamma_{4u}$ modes. In particular, for $\Gamma_4$ electronic states the vibronic energies satisfy

$$E(\Gamma_4)-E(\Gamma_5)=\tfrac{2}{3}[E(\Gamma_3)-E(\Gamma_1)] \tag{8}$$

for the $\Gamma_{4u}$ modes of frequency $\omega$, and

$$E'(\Gamma_4)-E'(\Gamma_5)=\tfrac{2}{3}[E'(\Gamma_3)-E'(\Gamma_1)] \tag{9}$$

for the $\Gamma_{4u}$ modes of frequency $\omega'$. A set of relations similar to (8) and (9) hold for $\Gamma_5$ electronic states, with the same correspondence (4) as before. These are formally the same relations as found between vibronic states involving $\Gamma_{5u}$ modes. We emphasize the fact that the vibronic energy differences arising from *each* of the $\Gamma_{4u}$ modes satisfy the same type of relation rather than the sum or average of corresponding prime and unprime energy levels satisfying such relations as one might have expected. We point out, however, that since the $\Gamma_{4u}$ modes do not have the simple mass dependence of the $\Gamma_{5u}$ modes, there is no simple mass dependence implicit in the vibronic energy levels or their differences (8) or (9).

## Case A: Zeeman Interaction Small Compared to Vibronic Interaction

Applied to $UCl_6^{2-}$ or $UBr_6^{2-}$ complexes, the situation that the Zeeman interaction is small compared to the vibronic interaction can only occur for the isolated complex ion or to very localized modes of the complex in some host crystal, not in an undoped crystal such as pure $Cs_2UBr_6$. The situation in pure crystals will be further discussed in a later section.

If the Zeeman interaction is small compared to the separation of the vibronic levels, then we need consider only the matrix of $V_{ev}$ within the threefold degenerate $\Gamma_{4u}$ vibronic states for transitions from the ground $\Gamma_1$ state, and also $\Gamma_{5u}$ vibronic states in other situations.

The $g$ values for the electronic state can be defined with the aid of an effective Hamiltonian $g\beta\mathbf{S}\cdot\mathbf{H}$, employing effective spin-1 matrices:

$$(\phi_1|S_z|\phi_1)=0,$$

$$(\phi_2|S_z|\phi_2)=-(\phi_3|S_z|\phi_3)=1$$

for $\Gamma_4$ electronic states, and a similar set of relations for $\Gamma_5$ electronic states, obtained by the replacement of $\psi_i$ for $\phi_i$.

It follows from the $\Gamma_4$ vibronic eigenfunctions in Table II (and also for $\Gamma_5$ vibronic states), built from

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[12] J. C. Lenander, Phys. Rev. **130**, 1033 (1963).

either $\Gamma_4$ or $\Gamma_5$ electronic states and one quantum of a $\Gamma_{4u}$ vibration, that the vibronic $g$ value is one-half of the parent electronic state $g$ value:

$$g_{\text{vibr}}=\tfrac{1}{2}g. \tag{10}$$

Similarly for $\Gamma_{5u}$ vibrations we find

$$g_{\text{vibr}}=-\tfrac{1}{2}g, \tag{11}$$

where the relative sign in (10) or (11) refers to whether or not the state labeled $\rho=2$ is raised or lowered in a magnetic field, which can be detected with circular polarization. The splitting of a pure electronic state is (in the vibronic state) shared equally by the $\Gamma_4$ and $\Gamma_5$ vibronic states, as evident from the wave functions in Table II, as the following particular example demonstrates for $\Gamma_4$ electronic states and $\Gamma_{5u}$ vibrations:

$$\begin{aligned} g_{\text{vibr}} &= (\Gamma_4\rho=2 \mid gS_z \mid \Gamma_4\rho=2) \\ &= \tfrac{1}{2}(\phi_3Q_1-\phi_1Q_2 \mid gS_z \mid \phi_3Q_1-\phi_1Q_2) \\ &= \tfrac{1}{2}(\phi_3 \mid gS_z \mid \phi_3) = -\tfrac{1}{2}g, \end{aligned}$$

where we have used the convention in Table II of representing the vibrational wave function with one quantum of vibration by its normal coordinate and omitting all other vibrational wave functions in their $n=0$ quantum state. These results, although illustrated for the $Z$ component of the effective-spin operator are, nevertheless, independent of relative orientation of molecule and field, i.e., the splitting into three equally spaced levels is isotropic.

The $\frac{1}{2}g$ results should be particularly interesting in paramagnetic resonance at $kT\simeq\hbar\omega$ since the condition of case A, Zeeman splitting small compared to vibronic splitting, is easier to achieve than for optical experiments which require higher magnetic fields.

### Case B: Zeeman Interaction Comparable to Vibronic Interaction

When the magnetic field is increased beyond case A, the symmetry is lowered, the splitting of the $\Gamma_4$ vibronic states becomes nonuniform and anisotropic due to matrix elements of the magnetic interaction between vibronic levels belonging to different $O_h$ irreducible representations, and also new lines can appear in the spectrum due to such mixing. The size of the matrices which must be considered varies from $9\times9$ to $2\times2$ or $3\times3$, depending on the magnetic field orientation relative to the molecule. Thus, for freely rotating molecules, the Zeeman spectrum may consist of broad lines which result from averages of the levels over all orientations of the molecule relative to the field. Local modes in a solid may provide molecules in fixed orientations resulting in sharp lines. We illustrate the matrices appropriate to a magnetic field along a fourfold axis of symmetry for $\Gamma_5$ electronic states and $\Gamma_{5u}$ modes. The symmetry of the Hamiltonian is reduced to $C_{4h}$. The following correlation table is useful in simplifying the matrices:

$$\begin{array}{llllll} O_h & \Gamma_5 & \rho=1 & \text{is a basis for} & \Gamma_2 & \text{of} \quad C_4 \\ & \Gamma_5 & \rho=2 & \text{is a basis for} & \Gamma_4 & \\ & \Gamma_5 & \rho=3 & \text{is a basis for} & \Gamma_3 & \\ & \Gamma_4 & \rho=1 & \text{is a basis for} & \Gamma_1 & \\ & \Gamma_4 & \rho=2 & \text{is a basis for} & \Gamma_4 & \\ & \Gamma_4 & \rho=3 & \text{is a basis for} & \Gamma_3 & \\ & \Gamma_3 & \rho=1 & \text{is a basis for} & \Gamma_2 & \\ & \Gamma_3 & \rho=2 & \text{is a basis for} & \Gamma_1 & \\ & \Gamma_1 & & \text{is a basis for} & \Gamma_1. & \end{array}$$

Thus, the matrices are all $2\times2$ except $\Gamma_1$, which is $3\times3$.

Thus for $C_{4h}$ symmetry the $V_{ev}$ interaction is diagonal in a basis of vibronic states belonging to our previous choice for the rows of an irreducible representation of $O_h$ and these diagonal elements are, in fact, already given by (2) with the replacements (4). Thus we need specify in detail only the matrix elements of the magnetic interaction. The resulting matrices are as follows: For $\Gamma_4$ of $C_4$:

$$\begin{pmatrix} E(\Gamma_5)-\frac{1}{2}(g\beta H) & -\frac{1}{2}(g\beta H) \\ -\frac{1}{2}(g\beta H) & E(\Gamma_4)-\frac{1}{2}(g\beta H) \end{pmatrix}, \tag{12}$$

For $\Gamma_3$ of $C_4$:

$$\begin{pmatrix} E(\Gamma_5)+\frac{1}{2}(g\beta H) & -\frac{1}{2}(g\beta H) \\ -\frac{1}{2}(g\beta H) & E(\Gamma_4)+\frac{1}{2}(g\beta H) \end{pmatrix}, \tag{13}$$

For $\Gamma_2$ of $C_4$:

$$\begin{pmatrix} E(\Gamma_5) & g\beta H \\ g\beta H & E(\Gamma_3) \end{pmatrix}, \tag{14}$$

For $\Gamma_1$ of $C_4$:

$$\begin{pmatrix} E(\Gamma_4) & g\beta H/\sqrt{3} & -\sqrt{2}g\beta H/\sqrt{3} \\ g\beta H/\sqrt{3} & E(\Gamma_3) & 0 \\ -\sqrt{2}g\beta H/\sqrt{3} & 0 & E(\Gamma_1) \end{pmatrix}. \tag{15}$$

The matrices can be readily solved for the eigenvalues. The limiting case A can be readily obtained from these matrices by neglecting the off-diagonal matrix elements. The limiting case C can be obtained by allowing each $E(\Gamma)$ to approach zero.

### Case C: Vibronic Interaction Small Compared to Zeeman Interaction—Crystals

In this case, one first diagonalizes the Zeeman energy in a basis of degenerate electronic states and adds the vibronic interaction to vibronic states already nondegenerate as a small perturbation. For vanishingly small vibronic interaction each vibronic line will therefore split with the *same g* value as the parent electronic level:

$$g_{\text{vibr}}=g, \qquad (16)$$

and the splitting is isotropic.

Case C is of importance in crystals even for those consisting of molecules or complex ions which, when free, would be case A. An example is $Cs_2UBr_6$, which is cubic and has octahedral $UBr_6{}^{2-}$ complexes, and even though the estimate of $V_{ev}$ splitting for the molecule is case A, as discussed above, the experimental situation follows (16) within experimental error. $Pr^{3+}$ and $Nd^{3+}$ in anhydrous trichloride hosts also satisfy (16), as shown by Cohen and Moos.[8] The reason in $Cs_2UBr_6$ and to some extent in the rare earths (in which $V_{ev}$ is smaller owing to smaller $V_c$) can be traced back to an effective reduction in $V_{ev}$ in the crystal for the type of vibronic spectral line observed, which is one of the fine structure lines due to peaks in the density of phonon states referred to in the Introduction. This fine structure is the only type of line in which one can hope to see the vibronic Zeeman splitting, as it is unlikely to be observed in a broad band.

The reduction of $V_{ev}$ splitting can be accounted for in a simple way. Suppose a vibronic line to be due to $N'$ phonons in an optical branch, each of which are presumed to be in a flat region of the phonon dispersion $E$ versus $k$. It is reasonable to assume that the $N'$ phonon modes have a range of $k$ vectors such that the unit cell eigenvectors are essentially the same for all $N'$ modes. This would in a sense account for the independence of the phonon energy $E$ of $k$ over this range. It is also reasonable to suppose that only the atoms within a Wigner-Seitz unit cell about a paramagnetic ion contribute to the electron-vibration interaction $V_{ev}$ between that ion and its neighbors. The electronic energy bands for 4*f* or 5*f* electronic states in lanthanide or actinide salts can be presumed to be extremely flat in $E$ versus $k$, so that we shall use the single-ion description of atomic states, just as if it were an impurity in its own lattice. Then vibronic states (built from linear combinations of products of electronic wave functions for the ion and vibrational wave functions for the lattice in a way analogous to the free ion in Table II) belonging to the same row of a particular irreducible representation will all have the same $V_{ev}$ matrix elements between any pair of such vibronic states, because the motion in the unit cell containing our paramagnetic ion is the same for each of the $N'$ modes.

Call this matrix element $a$. But $a=a_1/N$, where $a_1$ is the size of the interaction if the quantum of vibrational energy were localized within the unit cell, and $N$ is the number of unit cells and also the total number of $k$ vectors in the optical branch. We must diagonalize the $N'\times N'$ matrix, each matrix element of which is the same, namely $a$. The secular equation is

$$\operatorname{Det}\begin{pmatrix} a-E & a & \cdots & a \\ a & a-E & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ a & \cdots & & a-E \end{pmatrix}=0. \qquad (17)$$

It is easy to show by adding columns that the eigenvalues of (17) are

$$E=N'a=(N'/N)a_1$$

and

$$E=0 \qquad (N'-1)\text{-fold}. \qquad (18)$$

This is what we wished to prove. Note that for a perfectly flat $E$ versus $k$ throughout the entire Brillouin zone, $N'=N$ and $E=a_1$ as expected. For a pure undoped crystal it is easy to see how $N'/N$ would be small enough to reduce $V_{ev}$ from case A to case C. However, for localized modes obtained by doping paramagnetic ions in the proper host, one might expect to find the vibronic Zeeman effect to no longer reflect the Zeeman splitting of the parent electronic level but to be modified from it in a way in which one could learn about the density of states. In any case, it provides a test for the existence of localized modes.

An important consequence of the reduction factor produced by the relative density of states $N'/N$ is that, when localized modes are not present, the vibronic shifts as well as splittings are negligible, so that the peaks in the vibronic spectrum should directly reflect the peaks in the phonon density of states without appreciable modification by vibronic energy shifts and splittings.

On the other hand, an example[13] of the influence of localized modes on the electronic energy spectrum is that of the shift in the pure electronic level of a $Nd^{3+}$ or $Pr^{3+}$ ion in $LaF_3$ doped with $H^-$ ions replacing $F^-$. Actually the *difference* in shift when $H^-$ was replaced by $D^-$ was observed due to the electron-vibration interaction and the difference in zero-point amplitude between $H^-$ and $D^-$, which is large partly because of the relatively large percentage change in mass, and partly because the vibrations are localized.

## APPENDIX

The following matrix-element relations are a consequence of symmetry:

$$\begin{aligned}(\phi_2|W_1|\phi_3)&=-(\phi_3|W_1|\phi_2)\\&=(\phi_1|W_2|\phi_3)\\&=-(\phi_2|W_2|\phi_1)\\&=(\phi_1|W_3|\phi_2)\\&=-(\phi_3|W_3|\phi_1),\end{aligned}$$

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[13] G. D. Jones and R. A. Satten, Phys. Rev. **147**, 566 (1966).

$$\begin{aligned}
(\psi_2 \mid W_1 \mid \psi_3) &= -(\psi_3 \mid W_1 \mid \psi_2)\\
&= -(\psi_1 \mid W_2 \mid \psi_2)\\
&= -(\psi_3 \mid W_2 \mid \psi_1)\\
&= (\psi_1 \mid W_3 \mid \psi_3)\\
&= (\psi_2 \mid W_3 \mid \psi_1),\\
-\tfrac{1}{2}(\phi_1 \mid V_2 \mid \phi_2) &= (\phi_2 \mid V_2 \mid \phi_2)\\
&= (\phi_3 \mid V_2 \mid \phi_3)\\
&= (3)^{-1/2}(\phi_2 \mid V_1 \mid \phi_3)\\
&= (3)^{-1/2}(\phi_3 \mid V_1 \mid \phi_2),\\
-\tfrac{1}{2}(\psi_1 \mid V_2 \mid \psi_1) &= (\psi_2 \mid V_2 \mid \psi_2)\\
&= (\psi_3 \mid V_2 \mid \psi_3)\\
&= -(3)^{-1/2}(\psi_2 \mid V_1 \mid \psi_3)\\
&= -(3)^{-1/2}(\psi_3 \mid V_1 \mid \psi_2),
\end{aligned}$$

where the various functions transform as in Table II, and of course, similar relations hold for any other functions transforming in the same way.

The following vibrational matrix elements are useful $(Q_2{}^*=Q_3)$:

$$\begin{aligned}
(Q_1 \mid Q_1{}^2 \mid Q_1) &= 3\hbar/2\omega,\\
(Q_2 \mid Q_2Q_3 \mid Q_2) &= (Q_3 \mid Q_2Q_3 \mid Q_3)\\
&= (Q_2 \mid Q_2{}^2 \mid Q_3)\\
&= (Q_3 \mid Q_3{}^2 \mid Q_2)\\
&= \hbar\omega,\\
(Q_3 \mid Q_2{}^2 \mid Q_2) &= (Q_2 \mid Q_3{}^2 \mid Q_3)\\
&= (Q_2 \mid Q_2{}^2 \mid Q_2)\\
&= (Q_2 \mid Q_3{}^2 \mid Q_2)\\
&= (Q_3 \mid Q_2{}^2 \mid Q_3)\\
&= (Q_3 \mid Q_3{}^2 \mid Q_3) = 0,\\
(Q_1 \mid Q_1 \mid 0) &= (0 \mid Q_1 \mid Q_1)\\
&= (Q_2 \mid Q_2 \mid 0)\\
&= (Q_3 \mid Q_3 \mid 0)\\
&= (0 \mid Q_3 \mid Q_2)\\
&= (0 \mid Q_2 \mid Q_3)\\
&= (\hbar/2\omega)^{1/2},\\
(Q_2 \mid Q_3 \mid 0) &= (Q_3 \mid Q_2 \mid 0)\\
&= (0 \mid Q_2 \mid Q_2)\\
&= (0 \mid Q_3 \mid Q_3) = 0,\\
(00 \mid Q_2Q_3 \mid 00) &= (0 \mid Q_1{}^2 \mid 0)\\
&= \hbar/2\omega,
\end{aligned}$$

where normal coordinates in place of wave functions stand for the corresponding vibrational eigenfunction with one quantum of excitation, all other modes being assumed in the $n=0$ vibrational state, which is sometimes indicated explicitly by a zero. A similar convention holds for the following $\Gamma_{4u}$ vibrational modes $(q_2{}^*=-q_3)$:

$$\begin{aligned}
(q_1 \mid q_1{}^2 \mid q_1) &= 3\hbar/2\omega,\\
(q_2 \mid q_2q_3 \mid q_2) &= (q_3 \mid q_2q_3 \mid q_3)\\
&= (q_2 \mid q_2{}^2 \mid q_3)\\
&= (q_3 \mid q_3{}^2 \mid q_2)\\
&= -\hbar/\omega,\\
(q_3 \mid q_2{}^2 \mid q_2) &= (q_2 \mid q_3{}^2 \mid q_3)\\
&= (q_2 \mid q_2{}^2 \mid q_2)\\
&= (q_2 \mid q_3{}^2 \mid q_2)\\
&= (q_3 \mid q_2{}^2 \mid q_3)\\
&= (q_3 \mid q_3{}^2 \mid q_3) = 0,\\
(q_1 \mid q_1 \mid 0) &= (0 \mid q_1 \mid q_1)\\
&= (q_2 \mid q_2 \mid 0)\\
&= -(0 \mid q_2 \mid q_3)\\
&= -(0 \mid q_3 \mid q_2)\\
&= (\hbar/2\omega)^{1/2},\\
(q_2 \mid q_3 \mid 0) &= (q_3 \mid q_2 \mid 0)\\
&= (0 \mid q_2 \mid q_2)\\
&= (0 \mid q_3 \mid q_3) = 0,\\
(00 \mid q_2q_3 \mid 00) &= -\hbar/2\omega\\
&= -(0 \mid q_1 \mid 0).
\end{aligned}$$