

If the ground state of Ge^{77} were $g_{9/2}$, the beta-ray spectrum would have a forbidden shape ($\Delta j = \pm 2$, yes) and a larger value of $\log ft$. If the ground state of Ge^{77} is $G_{7/2}$ the spectral shape and value of $\log ft$ are consistent with a transition of the type $\Delta j = \pm 1$, yes. In addition, one can get an approximate idea of the half-life for gamma-ray emission by using the empirical formula of Goldhaber and Sunyar.¹ For a transition $\Delta I = 4$ ($p_{1/2}$ to $g_{9/2}$) one obtains 3×10^4 sec and for $\Delta I = 3$ ($p_{1/2}$ to $G_{7/2}$) one obtains < 1 sec for the half-life. The value $\Delta I = 3$ will allow the gamma-ray transition to compete with the 59-sec beta-decay whereas the transition $\Delta I = 4$ would make the gamma-ray transition extremely weak. From these two lines of evidence it is concluded that the ground state of Ge^{77} has the configuration $G_{7/2}$ and that the isomeric state ($p_{1/2}$) lies 380 kev above it.

* Supported by the joint program of the ONR and AEC.

¹ M. Goldhaber and A. W. Sunyar, Phys. Rev. 83, 906 (1951).

² J. R. Arnold and N. Sugarman, J. Chem. Phys. 15, 703 (1947).

³ R. Hofstadter and J. A. McIntyre, Phys. Rev. 80, 631 (1950).

Ions of Mass 19 from Water

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(Received November 8, 1951)

A RECENT paper¹ has shown that in the mass spectrometric determination of the HOD^+ ion of mass 19 present in ordinary water, high H_2O pressures can yield spurious mass 19 ions, presumably H_3O^+ , from the collision of H_2O^+ ions with H_2O molecules.

I have found that excess H_2 when present with water also yields much H_3O^+ in the mass spectrometer, and that the shape of its ionization probability function, as ionizing voltage is changed, is entirely different from the ionization curve for HOD^+ .

Figure 1 shows the magnitude of the ratio peak 19/peak 18. Curve (a) represents increasing amounts of water alone. Curve (b) is for similar amounts of water with added hydrogen, from a mixture of 98.2 percent H_2 and 1.8 percent H_2O , and shows how greatly the added H_2 increases peak 19. All these measurements were made at an ionizing voltage of 70 and an accelerating voltage of 2000.

Figure 2 gives variation of peak height, or positive ion current, as ionizing voltage is changed. Curve (1) is peak 19, HOD^+ from a mixture of about 50 percent H_2O and 50 percent D_2O . Curve (2) is peak 19, H_3O^+ from the mixture of H_2 and H_2O . The ion current at the maximum for H_3O^+ was 1.9×10^{-12} amps, and for HOD^+ , 1.1×10^{-11} amps.

The ionizing efficiency curve (1) is normal and like that for H_2O^+ and for D_2O^+ . Curve (2) for H_3O^+ is very unusual for ionizing efficiency, having a sharp maximum at 19 volts. It resembles excitation curves and leads to the suggestion that perhaps

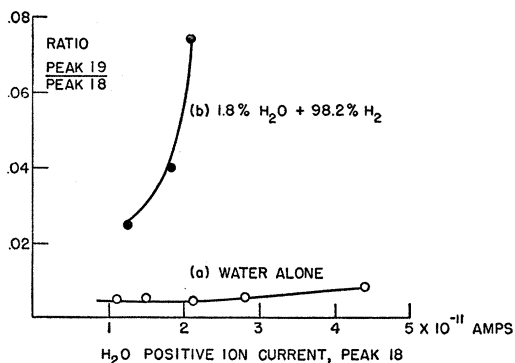


FIG. 1. Formation of ions of mass 19 by excess H_2 .

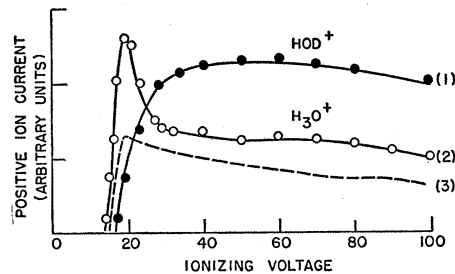


FIG. 2. Ionizing efficiency curves for H_3O^+ and HOD^+ .

there is first excitation and then ionization of a complex on second electron impact.

Niira² discussed H_2O excitation by electron impact, showing that excited H_2O molecules dissociate to the H atom and the OH radical in the excited $^2\Sigma^+$ state. The latter then makes a transition to the $^2\Pi$ ground state, emitting ultraviolet bands. Some of these OH radicals, according to Niira, rotate at abnormally high speeds corresponding to a temperature of 8000°K. This same paper gives the excitation curve, according to Hayakawa,³ to the $^2\Sigma^+$ state. This has a maximum near 20 volts and bears a marked resemblance to the ionizing efficiency curve for the H_3O^+ ion. Its shape is indicated by curve (3), Fig. 2.

The suggested process for formation of this ion then becomes: (1) Formation of an excited H_2O molecule which dissociates to give the OH radical. A portion decays to the ground state, but another part in the presence of H_2 can form the complex OH_3 in some unspecified state. (2) Electron impact then forms OH_3^+ from this. The ionizing efficiency curve for H_3O^+ might be considered a superposition of the excitation and ionization processes.

A practical test for distinguishing between the ions H_3O^+ and HOD^+ is to measure the ratio of mass 19 positive ion current at 20 volts ionizing potential to that at 70 volts. For H_3O^+ the ratio is 2.0; for HOD^+ the ratio is 0.45.

¹ Washburn, Berry, and Hall, Symposium on Mass Spectroscopy, Natl. Bur. Standards, Washington, D. C., Sept. 6-8, 1951. (To be published in a bound volume of symposium papers.)

² Kazuo Niira, J. Phys. Soc., Japan 4, 230 (1949).

³ G. Hayakawa, Proc. Phys.-Math. Soc., Japan 26, 78 (1944).

Experimentally Derived Configurational Coordinate Curves for Phosphors

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(Received November 12, 1951)

RECENTLY Williams¹ has attempted to put configurational coordinate curves on a quantitative basis by computing them for the system $\text{KCl}:\text{Tl}$ from fundamental properties of the ions involved. In this letter another technique will be described for evaluating these curves using experimental results as primary data.

The assumptions made here concerning the configurational coordinate curves are as follows:

- (1) The curves are parabolic.
- (2) The variation in energy of the system about its equilibrium position in either the ground or excited state is small compared with the energy band width in the corresponding absorption or emission band.
- (3) Transitions are made to parts of the parabolic configurational coordinate curves which can be represented closely by a straight line.
- (4) The system acts as a harmonic oscillator so that its energy levels and spatial distribution can be computed in the usual way. The population of the states is given by a Boltzmann distribution.

(5) The probability of a transition between the configurational coordinate curves is independent of position along the portions of the curves which lie within the experimental range.

Materials to which these assumptions apply will have Gaussian emission and absorption bands at low temperatures. This is observed in the emission of tungstate phosphors² and in the absorption of *F*-centers and thallium in alkali halides. Furthermore, the relative change in band width with temperature follows the form given in Fig. 1 where the curves are normalized at 300°K. The points for the absorption of KCl:Tl³ and the emission of MgWO₄² and Zn₂SiO₄:Mn²⁺⁴ follow the curves reasonably well and indicate vibrational frequencies of normal values.

Let the ground and excited states be represented as in Fig. 2 with force constants k_g and k_e , respectively, and let all quantities be given in cgs units. The absorption energy at the center of the band is given by

$$U_{\text{abs}} = U_0 + \frac{1}{2}k_e X_0^2, \quad (1)$$

and the energy of emission at the peak is

$$U_{\text{emis}} = U_0 - \frac{1}{2}k_g X_0^2. \quad (2)$$

From the relative change in width of the absorption band with temperature, the classical frequency of the system in its ground state can be evaluated as discussed previously. This frequency is given by

$$\nu_g = (1/2\pi)(k_g/M_g)^{1/2}, \quad (3)$$

where M_g is the effective mass of the vibrating system in its ground state. A similar equation, with subscripts *e*, can be applied to emission data. The band width in ergs, ΔE_A , of the low temperature absorption curve measured at the half-maximum points can be expressed as

$$\Delta E_A = 1.905 \times 10^{-13} k_e X_0 (\nu_g/k_g)^{1/2}, \quad (4)$$

and the band width of the emission curve at low temperature is

$$W = \frac{k_g k_e X_0 [k_e X_0 + k_g X_0 - 2(k_g k_e X_0^2 - 2k_g U_0 - 2k_e U_0)^{1/2}] + 2k_e U_0 (k_g - k_e)}{2(k_g - k_e)^2}. \quad (5)$$

The complete determination of the configurational coordinate curves requires that the six constants k_g , k_e , X_0 , U_0 , M_g , and M_e be evaluated from a possible seven pieces of data. If M_g and M_e are assigned values, only four constants need be evaluated.

In order to compare the configurational coordinate curves determined in this way with those computed by Williams, the equations have been solved for KCl:Tl assuming the absorption energy peak to be at 2475Å,³ the emission peak at 2980Å,⁵ the vibrational frequency in the ground state (see Fig. 1) as 4×10^{12} sec⁻¹, and the width of the low temperature absorption band to be 0.108 electron volts.³

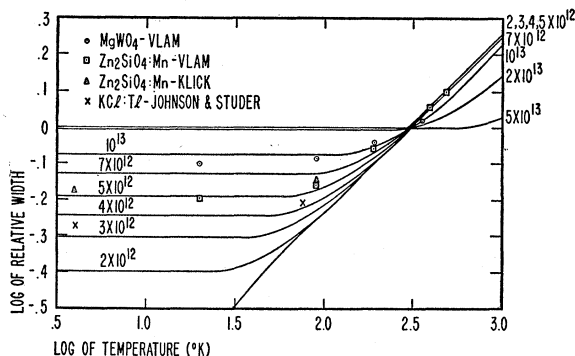


FIG. 1. Plot of the logarithm of the computed relative width at half-maximum of emission or absorption curves as a function of the logarithm of the temperature for various frequencies of vibration. Curves are normalized at 300°K.

TABLE I. Configurational coordinate constants for KCl:Tl.

Configurational coordinate constant	Theoretically derived values	Experimentally derived values
k_g	27×10^4	26.5×10^4
k_e	10.3×10^4	8.2×10^4
U_0	8.1×10^{-12}	7.7×10^{-12}
X_0	0.36×10^{-8}	0.28×10^{-8}

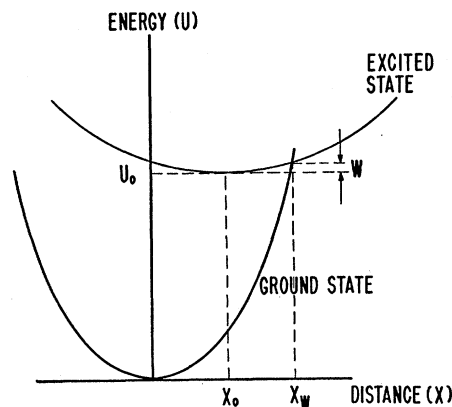


FIG. 2. Schematic configurational coordinate plot.

given by a similar equation with the subscripts *e* and *g* interchanged. The ground and excited state curves intersect at some energy W above the minimum of the excited state curve which can be computed from measurements on luminescence efficiency or decay rate. From Eqs. (1) and (2) W is given by

It is further assumed with Williams⁶ that only a single mode of vibration is important and that this corresponds to a synchronous and radial motion of the chlorine ions surrounding the thallium ion. The results of this analysis are given in Table I.

The agreement is surprising in view of the radically different approaches to the determination of the configurational coordinate curves and indicates, first, that the assumption of a single, radial vibratory mode produces results in agreement with experiment and, second, that the method described here may be used in the case of simple systems to evaluate configurational coordinates from experimental data.

¹ F. E. Williams, J. Chem. Phys. 19, 457 (1951).

² C. C. Vlam, Physica 15, 609 (1949).

³ P. D. Johnson and F. J. Studer, Phys. Rev. 82, 976 (1951).

⁴ C. C. Klick and J. H. Schulman, J. Opt. Soc. Am. 40, 509 (1950).

⁵ W. von Meyern, Z. Physik 61, 321 (1930).

⁶ F. E. Williams, Phys. Rev. 82, 281 (1951).

Protons and Deuterons from Li⁶+T Reactions

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THE interaction of tritons with Li⁶ may lead to the following exothermic reactions:¹

