fluence of the 1.35 cm line is negligible, and the contributions of other lines are dominant rather than residual. Figure 3 shows that there are some very strong resonances in the millimeter region, and that even in the valleys the absorption due to water vapor is so high as to make wave-lengths shorter than a millimeter or so useless for transmission except over exceedingly short distances. Incidentally, any modifications of the standard Lorentz theory such as we discussed previously will tend to make the absorption higher than shown in Fig. 3, especially in the valleys. Of course the opacity does not continue if the wave-length is reduced indefinitely. However, the opening up of the atmosphere to transmission occurs only when the frequency becomes high compared to the rotational frequencies of the water molecule, or in other words falls in the infra-red rather than microwave region.[22]

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[22] For a calculation of the absorption of water vapor in the infra-red region, see W. M. Elsasser, Astrophys. J. **87**, 497 (1938).

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Expected Microwave Absorption Coefficients of Water and Related Molecules*

GILBERT W. KING
Arthur D. Little, Inc., and Massachusetts Institute of Technology, Cambridge, Massachusetts

R. M. HAINER
Arthur D. Little, Inc.

AND PAUL C. CROSS
Brown University, Providence, Rhode Island

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The microwave absorption of water and related molecules is of interest for practical and theoretical reasons. Since these molecules are asymmetric rotors, the occurrence of lines is a matter of chance and the calculation of their intensities is rather difficult. The line strengths of all transitions of H_2O up to $J=6$ have been calculated exactly and the transformation matrices are given explicitly. Van Vleck has shown that the observed intensity of the $6_{16}-6_{23}$ radar line can be accounted for theoretically, by use of the calculated value of the line strength. The microwave absorption of HDO and D_2O is also predicted with the use of the dipole moment and half-width of H_2O which are presumably the same in the isotopic molecules. In addition, it is pointed out that HDO has components along both the least and intermediate axes of inertia. The selection rules for the former are quite different from the latter (obtaining in H_2O, D_2O), and give rise to transitions between levels which are components of doubly degenerate levels in the limiting case of the symmetric rotor. This splitting varies in magnitude so that lines of HDO should appear throughout the radio and microwave regions. One of these lines has been discovered at 0.7441 cm^{-1}, and is interpreted as the $5_{33}-5_{32}$ transition predicted at 0.79 cm^{-1}. The calculated absorption coefficient is 26×10^{-6} cm^{-1} which is in excellent agreement with the observed value of 30×10^{-6} cm^{-1}. The microwave absorption of H_2S and H_2Se is discussed, and it is pointed out that HDS and HDSe will also have many lines in this region.

INTRODUCTION

THE pure rotation spectra of gaseous molecules extend to the microwave region, where measurements are of value in determinations of molecular structure on account of the relatively great accuracy in which positions and absolute intensities of lines can be determined. The microwave absorption of asymmetric rotors is of particular interest because of the difficulties of analysis of their infra-red vibrational-rotational bands. The spectra of water and similar molecules are of primary interest because the small moments of inertia result in only a few

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lines appearing in the region, so that identification is relatively simple. The microwave spectra of heavier molecules will probably be quite complex, and identification of lines will necessitate elaborate experimentation, such as the determination of Stark effects and temperature coefficients. The three compounds H_2O, H_2S, H_2Se are considered here for various reasons. They form a family of closely related structure, of decreasing dipole moment. Their rotational energy levels are better known than for any other series. Theoretical factors affecting intensity and selection rules can be followed in the spectra of the isotopic molecules HDO, D_2O, etc., which are readily available. The calculation of the microwave absorption of H_2O was carried out by Van Vleck[1] because of its importance in radar. One of the difficult parts of the problem, namely the calculation of line strengths for transitions of the asymmetric rotor, was carried out by us independently, by matrix methods, and has been extended to account for the absorption of some related molecules which have recently been investigated.

In asymmetric-rotor molecules the spacing of energy levels does not follow a simple rule and the existence of permitted transitions in the microwave region accessible to present-day equipment is accidental. To predict or interpret microwave absorption it is necessary to determine all possible transitions between asymmetric-rotor levels about one wave number apart. Since weak lines can be detected, the calculations should be carried to high levels ($J \sim 12$ for water-like molecules) where the Boltzmann population is still appreciable.

The position of the lines depends on the differences between two relatively large numbers, the term values of the zero-vibrational state. These are not known from infra-red spectra with the accuracy to which their differences can be obtained in the microwave region. In fact, one of the purposes of making measurements in this region is to determine the differences in term values accurately. Term values are known for H_2O and D_2O, but for no other molecules of this type. The energy levels of the other molecules considered here have to be estimated from theory based on the rigid-rotor energy levels corrected for various distortions.

An expression for the absorption coefficient of a line in this region has recently been obtained.[2] For absorption at the resonance frequency ν (cm^{-1}) by a gas at partial pressure p (atm.) and absolute temperature T the coefficient is very nearly[3]

$$\alpha = (8\pi^2 N/3kTQ)\mu^2\nu^2 g e^{-E/kT}\Sigma|\Phi|^2 p/\Delta\nu \text{ cm}^{-1}. \quad (1)$$

A detailed discussion of the absorption is given in references 1 and 2.

Here N is Loschmidt's number corrected for temperature (so that Np is the number of molecules per cc in the light path), μ the permanent dipole of the rotor, Q the partition function at T°K, E the energy of the initial state. Weight factors due to nuclear spin are indicated by g, which has values for even and odd rotational states of 1 and 3 for H_2X, 6 and 6 for HDX, 6 and 3 for D_2X, X being the central atom. The average of these weights (namely their sum divided by the symmetry number) is used in computing Q. The factor $\Sigma|\Phi|^2$ is the line strength, defined as the squares of the elements of the direction-cosine matrices summed over the Zeeman components and three directions of space. Since the transition probabilities of the asymmetric rotor cannot be approximated by the symmetric-rotor values, especially when "forbidden" lines are considered, it is necessary to calculate the true values. A method of calculating line strengths and a table of values for certain degrees of asymmetry of the rotor have been given.[4] In effect then, the line strengths can be obtained accurately enough, although for the special case of H_2O the line strengths have been calculated for the particular degree of asymmetry in that molecule (Table I).

Thus all the quantities in (1) are known fairly accurately except for the mean free time between collisions, $1/(2\pi\Delta\nu)$. This factor arises from the line shape factor,[2] in which $\Delta\nu$ can be considered as the half-width at half-intensity. Simple kinetic

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[1] J. H. Van Vleck, Phys. Rev. **71**, 425 (1947).

[2] J. H. Van Vleck and V. F. Weisskopf, Rev. Mod. Phys. **17**, 227 (1945).

[3] Actually the peak occurs at the maximum of the function $\nu\nu_{ij}f(\nu_{ij}, \nu)$ of Eq. (13) of reference 2. A correction must be made if $\Delta\nu$ is not very much smaller than ν.

[4] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27 (1943) and **12**, 210 (1944).

theory predicts[5] and experiment indicates that $\Delta\nu$ is proportional to the total pressure P (atm.) so it can be written $P\Delta\nu_0$ where $\Delta\nu_0$ is the half-width for one atmosphere. The value of $\Delta\nu$ for H_2O in air has been determined[6] experimentally from an infra-red line as 0.11 cm^{-1}, and from microwave absorption itself as[7] $0.087\ (1+3.7p)$ cm^{-1}. For pure water vapor $\Delta\nu_0$ can be expected to be much higher, since polar water molecules probably have a much higher collision diameter than the non-polar oxygen and nitrogen molecules in air. This is demonstrated by the above equation obtained by Becker and Autler. From it the value of $\Delta\nu_0$ for pure water can be calculated as 0.41 cm^{-1}. Experiments with pure water vapor discussed below give a value of 0.357 cm^{-1}.

The values of $\Delta\nu_0$ for H_2S and H_2Se can be expected to be smaller than that for H_2O because of the smaller dipole moment of these molecules. Kinetic theory expresses $\Delta\nu_0$ as a product of certain well-known constants and the square of the "optical diameter" ρ,

$$\Delta\nu_0 = N(2kT/\pi)^{\frac{1}{2}}\rho^2((m+M)/mM)^{\frac{1}{2}} \tag{2}$$

(m and M being masses of the absorbing and colliding molecules, respectively) so that the uncertain part of (1) can be expressed as the ratio $(\mu/\rho)^2$ which will probably be fairly constant for the series H_2O, H_2S, H_2Se. This is a point worth consideration when experimental half-widths have been obtained. However, the values of $\Delta\nu_0$ for the isotopic molecules in each series will be very nearly the same. Thus exact *relative* intensities for lines of H_2O, HDO, D_2O and H_2S, HDS, D_2S, etc., can be calculated independently of uncertainties in $\Delta\nu_0$.

All calculations presented in Table II are based on a uniform value of $\Delta\nu_0 = 0.1$ cm^{-1}. Since this appears as a simple factor, the value of the absorption coefficient for any other estimate of $\Delta\nu_0$ can be found easily.

In this way the order of magnitude of the absorption can be predicted fairly well. The exact value of the absorption coefficient of Eq. (1), can be obtained, however, if any line is actually observed, since $\Delta\nu$ can be directly measured as the half-width. In other words, the product $\alpha\Delta\nu$ can be measured experimentally and compared with a theoretical quantity that can be calculated accurately.

The values of α given in Table II are for the pure gas, so that $p=P$; and as mentioned above, for $\Delta\nu_0 = 0.1$ cm^{-1}. The coefficient for mixtures, such as water vapor in air, or in the equilibrium mixture of H_2O, HDO, and D_2O, can be computed by multiplying the tabulated value by the appropriate ratio of partial to total pressure p/P.

Finally, it should also be pointed out that the tabulated values are computed with the predicted position, ν_{calc}. Since even in the best case, of H_2O, the position is not quite as calculated, the absorption coefficient should be corrected for the observed frequency by multiplying by $(\nu_{\text{obs}}/\nu_{\text{calc}})^2$.

A temperature of 14.5°C was used in the calculations corresponding to $kT = 200$ cm^{-1}. To find the absorption at any other temperature T a slight correction would have to be applied to allow for the change in various quantities appearing in (1), namely T itself, N, Q, $\Delta\nu$, and the Boltzmann factor. The first four give a factor of $(287.7/T)^3$ which is compensated by the Boltzmann factor to a degree dependent on the lower energy level.

H_2O

The positions of lines of water vapor in the microwave region can be estimated from the term values[8] of the ground state, and those lying above 0.1 cm are listed in Table II*A*. The practical importance of the absorption of water vapor in the radar region of one centimeter led us to compute the transition probabilities very precisely. The probabilities based on the theory of the rigid rotor are of sufficient accuracy.

A method of calculating transition probabilities for the asymmetric rotor has been given.[4] Briefly it depends on the transformation of the known direction-cosine matrices for the symmetric rotor by the orthonormal matrix which diagonalizes the Hamiltonian of the asymmetric rotor. For a

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[5] V. Weisskopf, Phys. Zeit. **34**, 1 (1933) and H. Margenau and W. W. Watson, Rev. Mod. Phys. **8**, 22 (1936).

[6] A. Adel, NDRC Report 320 and especially the supplement thereto.

[7] G. E. Becker and S. H. Autler, Phys. Rev. **70**, 300 (1946).

[8] H. M. Randall, D. M. Dennison, N. Ginsburg, and L. R. Weber, Phys. Rev. **52**, 160 (1937), and D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

TABLE I. Line strengths of all possible transitions between levels (through $J=6$) of the water-vapor molecule (dipole moment parallel to the axis of intermediate moment of inertia). The transitions are classified by sub-branches[4] which head the column in which the initial level can be found (identified by $J_{K_{-1},K_1;\tau}$) and whose final level is in the adjacent column. Thus each value in column 3 corresponds to two transitions, whose lower levels are in columns 1 and 2, respectively.

Transition		Exact value	Exact minus 4 pt. inter.
${}^{b,e}Q_{1,\bar{1}}$	${}^{b,e}Q_{\bar{1},1}$		
$1_{0,1;-1}$	$1_{1,0;1}$	1.5000	.0000
$2_{1,1;0}$	$2_{2,0;2}$	1.2594	−.0010
$3_{2,1;1}$	$3_{3,0;3}$	1.0921	−.0002
$4_{3,1;2}$	$4_{4,0;4}$	1.0883	.0059
$5_{4,1;3}$	$5_{5,0;5}$	1.1011	.0051
$6_{5,1;4}$	$6_{6,0;6}$	1.1117	.0034
$2_{0,2;-2}$	$2_{1,1;0}$	2.0739	.0010
$3_{1,2;-1}$	$3_{2,1;1}$	2.5434	.0073
$4_{2,2;0}$	$4_{3,1;2}$	2.1659	−.0231
$5_{3,2;1}$	$5_{4,1;3}$	2.0658	−.0106
$6_{4,2;2}$	$6_{5,1;4}$	2.0900	.0139
$3_{0,3;-3}$	$3_{1,2;-1}$	2.1809	−.0077
$4_{1,3;-2}$	$4_{2,2;0}$	3.6547	.0221
$5_{2,3;-1}$	$5_{3,2;1}$	3.4462	.0184
$6_{3,3;0}$	$6_{4,2;2}$	3.0719	−.0801
$4_{0,4;-4}$	$4_{1,3;-2}$	2.0369	−.0068
$5_{1,4;-3}$	$5_{2,3;-1}$	4.2239	−.0440
$6_{2,4;-2}$	$6_{3,3;0}$	4.8520	.1564
$5_{0,5;-5}$	$5_{1,4;-3}$	1.8994	.0325
$6_{1,5;-4}$	$6_{2,4;-2}$	4.2180	−.1800
$6_{0,6;-6}$	$6_{1,5;-4}$	1.8411	.0870
${}^{b,o}Q_{1,\bar{1}}$	${}^{b,o}Q_{\bar{1},1}$		
$2_{1,2;-1}$	$2_{2,1;1}$	0.8333	.0000
$3_{2,2;0}$	$3_{3,1;2}$	1.0360	−.0002
$4_{3,2;1}$	$4_{4,1;3}$	1.0831	−.0003
$5_{4,2;2}$	$5_{5,1;4}$	1.1007	.0005
$6_{5,2;3}$	$6_{6,1;5}$	1.1117	.0015
$3_{1,3;-2}$	$3_{2,2;0}$	1.2973	.0002
$4_{2,3;-1}$	$4_{3,2;1}$	1.8497	.0003
$5_{3,3;0}$	$5_{4,2;2}$	2.0248	−.0019
$6_{4,3;1}$	$6_{5,2;3}$	2.0855	−.0041
$4_{1,4;-3}$	$4_{2,3;-1}$	1.5659	−.0002
$5_{2,4;-2}$	$5_{3,3;0}$	2.4942	.0012
$6_{3,4;-1}$	$6_{4,3;1}$	2.8814	.0041
$5_{1,5;-4}$	$5_{2,4;-2}$	1.7088	.0001
$6_{2,5;-3}$	$6_{3,4;-1}$	2.9653	−.0054
$6_{1,6;-5}$	$6_{2,5;-3}$	1.7784	.0039
${}^{b,e}R_{1,1}$	${}^{b,o}P_{\bar{1},\bar{1}}$		
$0_{0,0;0}$	$1_{1,1;0}$	1.0000	.0000
$1_{0,1;-1}$	$2_{1,2;-1}$	1.5000	.0000
$2_{0,2;-2}$	$3_{1,3;-2}$	2.1571	−.0001
$3_{0,3;-3}$	$4_{1,4;-3}$	3.0069	.0021
$4_{0,4;-4}$	$5_{1,5;-4}$	3.9767	−.0016
$5_{0,5;-5}$	$6_{1,6;-5}$	4.9837	−.0152
$1_{1,0;1}$	$2_{2,1;1}$	1.5000	.0000
$2_{1,1;0}$	$3_{2,2;0}$	1.6667	.0000
$3_{1,2;-1}$	$4_{2,3;-1}$	1.9708	−.0005
${}^{b,e}R_{1,1}$	${}^{b,o}P_{\bar{1},\bar{1}}$		
$4_{1,3;-2}$	$5_{2,4;-2}$	2.4447	−.0032
$5_{1,4;-3}$	$6_{2,5;-3}$	3.1314	.0073
$2_{2,0;2}$	$3_{3,1;2}$	2.3947	.0004
$3_{2,1;1}$	$4_{3,2;1}$	2.3195	−.0010
$4_{2,2;0}$	$5_{3,3;0}$	2.3220	−.0022
$5_{2,3;-1}$	$6_{3,4;-1}$	2.4490	−.0020
$3_{3,0;3}$	$4_{4,1;3}$	3.3931	−.0005
$4_{3,1;2}$	$5_{4,2;2}$	3.2701	.0038
$5_{3,2;1}$	$6_{4,3;1}$	3.1529	.0024
$4_{4,0;4}$	$5_{5,1;4}$	4.3970	−.0014
$5_{4,1;3}$	$6_{5,2;3}$	4.2670	.0007
$5_{5,0;5}$	$6_{6,1;5}$	5.3998	−.0016
${}^{b,o}R_{1,\bar{1}}$	${}^{b,e}P_{\bar{1},1}$		
$1_{1,1;0}$	$2_{2,0;2}$	1.2444	.0006
$2_{2,1;1}$	$3_{3,0;3}$	2.3363	−.0302
$3_{3,1;2}$	$4_{4,0;4}$	3.3904	−.0025
$4_{4,1;3}$	$5_{5,0;5}$	4.3968	−.0025
$5_{5,1;4}$	$6_{6,0;6}$	5.3998	−.0021
$2_{1,2;-1}$	$3_{2,1;1}$	0.9225	−.0041
$3_{2,2;0}$	$4_{3,1;2}$	2.1653	.0078
$4_{3,2;1}$	$5_{4,1;3}$	3,2505	.0030
$5_{4,2;2}$	$6_{5,1;4}$	4.2648	−.0061
$3_{1,3;-2}$	$4_{2,2;0}$	0.6050	−.0019
$4_{2,3;-1}$	$5_{3,2;1}$	1.8396	−.0065
$5_{3,3;0}$	$6_{4,2;2}$	3.0678	.0263
$4_{1,4;-3}$	$5_{2,3;-1}$	0.3804	.0171
$5_{2,4;-2}$	$6_{3,3;0}$	1.4022	−.0427
$5_{1,5;-4}$	$6_{2,4;-2}$	0.2494	.0410
${}^{b,e}R_{3,\bar{1}}$	${}^{b,o}P_{\bar{3},1}$		
$2_{0,2;-2}$	$3_{3,1;2}$	0.0133	−.0003
$3_{1,2;-1}$	$4_{4,1;3}$	0.0045	.0006
$4_{2,2;0}$	$5_{5,1;4}$	0.0020	.0012
$5_{3,2;1}$	$6_{6,1;5}$	0.0013	.0010
$3_{0,3;-3}$	$4_{3,2;1}$	0.0512	.0009
$4_{1,3;-2}$	$5_{4,2;2}$	0.0231	−.0031
$5_{2,3;-1}$	$6_{5,2;3}$	0.0089	.0007
$4_{0,4;-4}$	$5_{3,3;0}$	0.0966	.0033
$5_{1,4;-3}$	$6_{4,3;1}$	0.0708	−.0019
$5_{0,5;-5}$	$6_{3,4;-1}$	0.1240	.0010
${}^{b,e}Q_{3,\bar{3}}$	${}^{b,e}Q_{\bar{3},3}$		
$3_{0,3;-3}$	$3_{3,0;3}$	0.0168	.0004
$4_{1,3;-2}$	$4_{4,0;4}$	0.0059	−.0013
$5_{2,3;-1}$	$5_{5,0;5}$	0.0018	−.0001
$6_{3,3;0}$	$6_{6,0;6}$	0.0008	.0007
${}^{b,e}Q_{3,\bar{3}}$	${}^{b,e}Q_{\bar{3},3}$		
$4_{0,4;-4}$	$4_{3,1;2}$	0.0483	.0031
$5_{1,4;-3}$	$5_{4,1;3}$	0.0317	−.0004
$6_{2,4;-2}$	$6_{5,1;4}$	0.0104	−.0053
$5_{0,5;-5}$	$5_{3,2;1}$	0.0631	−.0011
$6_{1,5;-4}$	$6_{4,2;2}$	0.0858	.0123
$6_{0,6;-6}$	$6_{3,3;0}$	0.0514	−.0084
${}^{b,o}Q_{3,\bar{3}}$	${}^{b,o}Q_{\bar{3},3}$		
$4_{1,4;-3}$	$4_{4,1;3}$	0.0012	.0000
$5_{2,4;-2}$	$5_{5,1;4}$	0.0011	−.0001
$6_{3,4;-1}$	$6_{6,1;5}$	0.0008	−.0001
$5_{1,5;-4}$	$5_{4,2;2}$	0.0036	.0000
$6_{2,5;-3}$	$6_{5,2;3}$	0.0044	.0000
$6_{1,6;-5}$	$6_{4,3;1}$	0.0059	.0001
${}^{b,o}R_{3,\bar{3}}$	${}^{b,e}P_{\bar{3},3}$		
$3_{1,3;-2}$	$4_{4,0;4}$	0.0017	.0000
$4_{2,3;-1}$	$5_{5,0;5}$	0.0016	−.0001
$5_{3,3;0}$	$6_{6,0;6}$	0.0012	−.0001
$4_{1,4;-3}$	$5_{4,1;3}$	0.0048	.0002
$5_{2,4;-2}$	$6_{5,1;4}$	0.0056	−.0003
$5_{1,5;-4}$	$6_{4,2;2}$	0.0076	.0005
${}^{b,e}R_{5,\bar{3}}$	${}^{b,o}P_{\bar{5},3}$		
$4_{0,4;-4}$	$5_{5,1;4}$	0.0001	.0001
$5_{1,4;-3}$	$6_{6,1;5}$	0.0000	.0000
$5_{0,5;-5}$	$6_{5,2;3}$	0.0002	.0000
${}^{b,o}R_{\bar{1},1}$	${}^{b,e}P_{1,\bar{1}}$		
$1_{1,1;0}$	$2_{0,2;-2}$	0.7557	−.0005
$2_{1,2;-1}$	$3_{0,3;-3}$	1.7441	.0040
$3_{1,3;-2}$	$4_{0,4;-4}$	2.8374	.0019
$4_{1,4;-3}$	$5_{0,5;-5}$	3.9184	−.0172
$5_{1,5;-4}$	$6_{0,6;-6}$	4.9646	−.0417
$2_{2,1;1}$	$3_{1,2;-1}$	0.3003	.0002
$3_{2,2;0}$	$4_{1,3;-2}$	0.8347	−.0078
$4_{2,3;-1}$	$5_{1,4;-3}$	1.6407	.0066
$5_{2,4;-2}$	$6_{1,5;-4}$	2.6812	.0425
$3_{3,1;2}$	$4_{2,2;0}$	0.1613	.0023
$4_{3,2;1}$	$5_{2,3;-1}$	0.4349	−.0032
$5_{3,3;0}$	$6_{2,4;-2}$	0.8606	−.0253
$4_{4,1;3}$	$5_{3,2;1}$	0.1193	.0028
$5_{4,2;2}$	$6_{3,3;0}$	0.3030	.0059
$5_{5,1;4}$	$6_{4,2;2}$	0.0990	.0023
${}^{b,e}R_{\bar{1},3}$	${}^{b,o}P_{1,\bar{3}}$		
$2_{2,0;2}$	$3_{1,3;-2}$	0.1015	.0000

Table I.—*Continued.*

Transition		Exact value	Exact minus 4 pt. inter.
$^{b,e}R\bar{1},3$	$^{b,o}P1,\bar{3}$		
$3_{2,1;1}$	$4_{1,4;-3}$	0.1224	−.0022
$4_{2,2;0}$	$5_{1,5;-4}$	0.0891	.0014
$5_{2,3;-1}$	$6_{1,6;-5}$	0.0549	.0131
$3_{3,0;3}$	$4_{2,3;-1}$	0.1316	.0003
$4_{3,1;2}$	$5_{2,4;-2}$	0.2622	.0026
$5_{3,2;1}$	$6_{2,5;-3}$	0.3117	−.0064
$4_{4,0;4}$	$5_{3,3;0}$	0.1165	−.0006
$5_{4,1;3}$	$6_{3,4;-1}$	0.2784	.0019
$5_{5,0;5}$	$6_{4,3;1}$	0.0987	−.0006
$^{b,o}R\bar{3},3$	$^{b,e}P3,\bar{3}$		
$3_{3,1;2}$	$4_{0,4;-4}$	0.0042	.0001
$4_{3,2;1}$	$5_{0,5;-5}$	0.0112	.0002
$5_{3,3;0}$	$6_{0,6;-6}$	0.0162	−.0007
$4_{4,1;3}$	$5_{1,4;-3}$	0.0020	−.0001
$5_{4,2;2}$	$6_{1,5;-4}$	0.0099	.0009
$5_{5,1;4}$	$6_{2,4;-2}$	0.0005	−.0002
$^{b,e}R\bar{3},5$	$^{b,o}P3,\bar{5}$		
$4_{4,0;4}$	$51,5;-4$	0.0002	.0000
$5_{4,1;3}$	$61,6;-5$	0.0006	.0000
$5_{5,0;5}$	$62,5;-3$	0.0002	.0000
$^{b,e}Q5,\bar{5}$	$^{b,e}Q\bar{5},5$		
$5_{0,5;-5}$	$5_{5,0;5}$	0.0000	.0000
$6_{0,6;-6}$	$6_{5,1;4}$	0.0002	.0001
$6_{1,5;-4}$	$6_{6,0;6}$	0.0000	−.0001
$^{b,o}Q5,\bar{5}$	$^{b,o}Q\bar{5},5$		
$6_{1,6;-5}$	$6_{6,1;5}$	0.0000	.0000
$^{b,o}R5,\bar{5}$	$^{b,e}P\bar{5},5$		
$5_{1,5;-4}$	$6_{6,0;6}$	0.0000	.0000
$^{b,o}R\bar{5},5$	$^{b,e}P5,\bar{5}$		
$5_{5,1;4}$	$6_{0,6;-6}$	0.0000	.0000

given degree of asymmetry, κ, the elements of this orthonormal matrix can be computed rather simply from the successive convergents of the continued fractions whose roots are the reduced (rigid-rotor) energy levels, $E(\kappa)$, although these are of no value in themselves since the term values of H_2O are known. Because of their importance in defining the orthonormal transformation, used in the computation of transition probabilities, and their use in the more general theory of vibration-rotation interaction, the $E(\kappa)$ for water are tabulated for convenience (Table III) together with the elements of the orthonormal matrices (Table IV) for all levels up to and including $J=6$. The matrices as given were tested by applying them to the Hamiltonian (in the form[4] of Type II^r). The non-diagonal elements were zero, and the diagonal gave the correct values of $E(\kappa)$, with an error in the fifth decimal of 2 or 3 for low J, rising to 50 in the case of the fourth order matrix of $J=6$.

As pointed out in reference 8 the exact values of rigid-rotor moments used in any such calculation have no meaning in the general theory, but form the basis of a framework on which elaborations can be added. The value of κ used was -0.436426, corresponding exactly to the moments used by Randall, Dennison, Ginsburg, and Weber[8] in their rigid-rotor calculations. The elements of the direction-cosine matrices were squared and summed over the Zeeman components and three directions in space to give the line strengths. Table I gives the values of the line strengths of all possible transitions in the pure rotation spectrum of water up to $J=6$ as calculated by the exact method (i.e., for the above value of κ).

Since the calculation of the orthonormal transformation matrix for a given molecule is tedious, the possibility of interpolating the table of line strengths previously given for $\kappa=\pm 1$, ± 0.5, 0 was investigated by comparing the four-point interpolated values for $\kappa=-0.436$ with the exact values found for water. The "true" minus interpolated values of the line strength are given in column 4 of Table I. Where the error is largest, the line strengths change very rapidly with κ. In these cases interpolation of the logarithms of the line strengths gives an adequate value. For example, the error in the case of the well-known $^{b,e}R\bar{1},3$ line[9] $6_{1,6;-5}-5_{2,3;-1}$ is 0.0131. A four-point interpolation of the logarithms reduces the error to 0.0014. The errors in column 4 were used to indicate the precautions to be taken in interpolating the line strength for the other molecules discussed in this paper.

No difficulty arises in computing the other factors in (1), except for the half-width, which, however, is obtained experimentally. Only one line will appear in the region at present open to experimental investigation. As is well known,

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[9] The first two subscripts refer to the absolute values of K for the level in each of the two limiting cases of (prolate and oblate) symmetric rotors. This notation has a descriptive value discussed in the case of HDO. The difference between them is the commonly used τ-value, given as the third subscript.

TABLE II. Predicted absorption lines in the microwave regions. The absorption coefficient, α, is calculated for the predicted position ν and for $\Delta\nu_0=0.1$ cm^{-1}.

Sub-branch	Quantum number		Term values		Position (cm^{-1})	Line strength	α (10^{-6} cm^{-1})
	Upper	Lower	Upper	Lower			
			(*A*) H_2O				
${}^{b,e}R\bar{1},3$	$6_{1,6;-5}$	$5_{2,3;-1}$	447.17	446.39	0.78	.0549	37.83
${}^{b,e}R\bar{1},3$	$3_{1,3;-2}$	$2_{2,0;2}$	142.30	136.15	6.15	.1015	6838
${}^{b,e}R\bar{1},3$	$10_{2,9;-7}$	$9_{3,6;-3}$	1293.80	1283.02	10.78	.0870	174.7
${}^{b,e}R\bar{1},3$	$5_{1,5;-4}$	$4_{2,2;0}$	326.50	315.70	10.80	.0891	7544
			(*B*) D_2O				
${}^{b,o}R\bar{1},1$	$5_{3,2;1}$	$4_{4,1;3}$	269.34	269.03	0.31	.1136	5.04
${}^{b,e}R\bar{1},3$	$3_{1,3;-2}$	$2_{2,0;2}$	74.58	74.03	0.55	.1145	85.1
${}^{b,e}P1,\bar{1}$	$8_{7,2;5}$	$9_{6,3;3}$	880.18	879.50	0.68	.1900	1.92
${}^{b,o}P1,\bar{3}$	$8_{7,1;6}$	$9_{6,4;2}$	880.18	879.48	0.70	.1902	4.07
${}^{b,o}P1,\bar{3}$	$4_{4,0;4}$	$5_{3,3;0}$	269.04	267.41	1.63	.1133	281
${}^{b,e}R\bar{1},3$	$4_{2,3;-1}$	$3_{3,0;3}$	158.29	156.46	1.83	.1328	361
${}^{b,e}R\bar{1},3$	$6_{1,6;-5}$	$5_{2,3;-1}$	232.60	230.47	2.13	.0919	234
${}^{b,e}R\bar{1},3$	$8_{5,4;1}$	$7_{6,1;5}$	671.50	668.83	2.67	.2138	95.5
${}^{b,o}R\bar{1},1$	$8_{5,3;2}$	$7_{6,2;4}$	671.60	668.83	2.77	.2132	205
${}^{b,o}P1,\bar{3}$	$9_{8,1;7}$	$10_{7,4;3}$	1118.56	1115.45	3.11	.1713	11.1
${}^{b,e}P1,\bar{1}$	$9_{8,2;6}$	$10_{7,3;4}$	1118.56	1115.45	3.11	.1713	22.3
${}^{b,e}R\bar{1},3$	$11_{2,10;-8}$	$10_{3,7;-4}$	794.33	791.02	3.31	.1020	76.1
${}^{b,o}P1,\bar{3}$	$6_{2,4;-2}$	$7_{1,7;-6}$	308.69	305.32	3.37	.0599	525
${}^{b,o}P1,\bar{3}$	$10_{9,1;8}$	$11_{8,4;4}$	1383.12	1378.56	4.56	.1557	11.7
${}^{b,e}P1,\bar{1}$	$10_{9,2;7}$	$11_{8,3;5}$	1383.12	1378.56	4.56	.1557	5.84
${}^{b,o}P1,\bar{3}$	$11_{10,1;9}$	$12_{9,4;5}$	1672.71	1668.15	4.56	.1428	1.26
${}^{b,e}P1,\bar{1}$	$11_{10,2;8}$	$12_{9,3;6}$	1672.71	1668.15	4.56	.1428	2.52
			(*C*) HDO				
${}^{a,o}Q0,\bar{1}$	$4_{4,0;4}$	$4_{4,1;3}$	405.19	405.19	0.00	7.1950	(498)[a]
${}^{a,o}Q0,\bar{1}$	$5_{5,0;5}$	$5_{5,1;4}$	623.35	623.35	0.00	9.1619	(213)
${}^{a,o}Q0,\bar{1}$	$6_{5,1;4}$	$6_{5,2;3}$	716.88	716.88	0.00	7.7244	(113)
${}^{a,o}Q0,\bar{1}$	$6_{6,0;6}$	$6_{6,1;5}$	888.28	888.28	0.00	11.1382	(68.9)
${}^{a,o}Q0,\bar{1}$	$7_{5,2;3}$	$7_{5,3;2}$	826.22	826.22	0.00	6.6753	(56.3)
${}^{a,o}Q0,\bar{1}$	$7_{6,1;5}$	$7_{6,2;4}$	997.34	997.34	0.00	9.6292	(34.5)
${}^{a,o}Q0,\bar{1}$	$7_{7,0;7}$	$7_{7,1;6}$	1199.96	1199.96	0.00	13.1205	(17.1)
${}^{a,o}Q0,\bar{1}$	$8_{6,2;4}$	$8_{6,3;3}$	1122.20	1122.20	0.00	8.4779	(16.3)
${}^{a,o}Q0,\bar{1}$	$8_{7,1;6}$	$8_{7,2;5}$	1324.58	1324.58	0.00	11.5106	(8.0)
${}^{a,o}Q0,\bar{1}$	$8_{8,0;8}$	$8_{8,1;7}$	1558.39	1558.39	0.00	15.0937	(3.27)
${}^{a,o}Q0,\bar{1}$	$9_{6,3;3}$	$9_{6,4;2}$	1262.92	1262.92	0.00	7.5516	(7.17)
${}^{a,o}Q0,\bar{1}$	$9_{7,2;5}$	$9_{7,3;4}$	1464.96	1464.96	0.00	10.2371	(3.54)
${}^{a,o}Q0,\bar{1}$	$9_{8,1;7}$	$9_{8,2;6}$	1698.56	1698.56	0.00	13.4556	(1.45)
${}^{a,o}Q0,\bar{1}$	$9_{9,0;9}$	$9_{9,1;8}$	1963.58	1963.58	0.00	17.0830	(0.49)
${}^{a,o}Q0,\bar{1}$	$10_{7,3;4}$	$10_{7,4;3}$	1621.19	1621.19	0.00	9.2432	(1.46)
${}^{a,o}Q0,\bar{1}$	$10_{8,2;6}$	$10_{8,3;5}$	1854.49	1854.49	0.00	12.1107	(0.60)
${}^{a,o}Q0,\bar{1}$	$10_{9,1;8}$	$10_{9,2;7}$	2119.30	2119.30	0.00	15.4105	(0.20)
${}^{a,o}Q0,\bar{1}$	$10_{10,0;10}$	$10_{10,1;9}$	2415.52	2415.52	0.00	19.0743	(0.00)
${}^{a,o}Q0,\bar{1}$	$11_{7,4;3}$	$11_{7,5;2}$	1793.30	1793.30	0.00	8.5070	(0.57)
${}^{a,o}Q0,\bar{1}$	$11_{8,3;5}$	$11_{8,4;4}$	2026.22	2026.22	0.00	11.0034	(0.23)
${}^{a,o}Q0,\bar{1}$	$11_{9,2;7}$	$11_{9,3;6}$	2290.77	2290.77	0.00	14.0118	(0.078)
${}^{a,o}Q0,\bar{1}$	$11_{10,1;9}$	$11_{10,2;8}$	2586.81	2586.81	0.00	17.3729	(0.00)
${}^{a,o}Q0,\bar{1}$	$11_{11,0;11}$	$11_{11,1;10}$	2914.22	2914.22	0.00	21.0670	(0.00)
${}^{a,o}Q0,\bar{1}$	$12_{8,4;4}$	$12_{8,5;3}$	2213.83	2213.83	0.00	10.1401	(0.083)
${}^{a,o}Q0,\bar{1}$	$12_{9,3;6}$	$12_{9,4;5}$	2478.02	2478.02	0.00	12.8206	(0.00)
${}^{a,o}Q0,\bar{1}$	$12_{10,2;8}$	$12_{10,3;7}$	2773.81	2773.81	0.00	15.9295	(0.00)
${}^{a,o}Q0,\bar{1}$	$12_{11,1;10}$	$12_{11,2;9}$	3101.05	3101.05	0.00	19.3408	(0.00)
${}^{a,o}Q0,\bar{1}$	$12_{12,0;12}$	$12_{12,1;11}$	3459.66	3459.66	0.00	23.0608	(0.00)
${}^{a,o}Q0,\bar{1}$	$5_{4,1;3}$	$5_{4,2;2}$	483.17	483.16	0.01	5.8526	0.027
${}^{a,o}Q0,\bar{1}$	$12_{7,5;2}$	$12_{7,6;1}$	1981.42	1981.41	0.01	7.9559	0.00
${}^{a,o}Q0,\bar{1}$	$10_{6,4;2}$	$10_{6,5;1}$	1419.61	1419.59	0.02	6.9270	0.001
${}^{a,o}Q0,\bar{1}$	$3_{3,0;3}$	$3_{3,1;2}$	233.79	233.76	0.03	5.2440	0.77
${}^{a,o}Q0,\bar{1}$	$8_{5,3;2}$	$8_{5,4;1}$	951.50	951.45	0.05	5.8688	0.066
${}^{a,o}Q0,\bar{1}$	$11_{6,5;1}$	$11_{6,6;0}$	1592.37	1592.31	0.06	6.3911	0.004
${}^{a,o}Q0,\bar{1}$	$6_{4,2;2}$	$6_{4,3;1}$	577.07	576.97	0.10	4.9212	1.44
${}^{a,o}Q0,\bar{1}$	$9_{5,4;1}$	$9_{5,5;0}$	1092.82	1092.70	0.12	5.1924	0.17
${}^{a,o}Q0,\bar{1}$	$12_{6,6;0}$	$12_{6,7;-1}$	1781.33	1781.19	0.14	5.8191	0.008
${}^{a,o}Q0,\bar{1}$	$4_{3,1;2}$	$4_{3,2;1}$	296.34	296.15	0.19	4.0238	17.4
${}^{a,o}Q0,\bar{1}$	$7_{4,3;1}$	$7_{4,4;0}$	687.03	686.70	0.33	4.1949	7.7
${}^{a,o}Q0,\bar{1}$	$2_{2,0;2}$	$2_{2,1;1}$	109.29	108.95	0.34	3.3168	117
${}^{a,o}Q0,\bar{1}$	$10_{5,5;0}$	$10_{5,6;-1}$	1250.41	1250.05	0.36	4.7379	0.62
${}^{a,o}Q0,\bar{1}$	$5_{3,2;1}$	$5_{3,3;0}$	375.06	374.27	0.79	3.2083	162

TABLE II.—*Continued.*

Sub-branch	Quantum number		Term values		Position (cm^{-1})	Line strength	α ($10^{-6}\ \text{cm}^{-1}$)
	Upper	Lower	Upper	Lower			
${}^{a,o}Q0,\bar{1}$	$8_{4,4;0}$	$8_{4,5;-1}$	813.38	812.44	0.94	3.5554	28.4
${}^{a,o}Q0,\bar{1}$	$11_{5,6;-1}$	$11_{5,7;-2}$	1424.54	1423.60	0.94	4.0958	1.54
${}^{a,o}Q0,\bar{1}$	$3_{2,1;1}$	$3_{2,2;0}$	156.98	155.28	1.70	2.2592	1580
${}^{a,o}Q0,\bar{1}$	$12_{5,7;-2}$	$12_{5,8;-3}$	1615.54	1613.37	2.17	3.4302	2.66
${}^{a,o}Q0,\bar{1}$	$6_{3,3;0}$	$6_{3,4;-1}$	470.40	468.14	2.26	2.5695	663
${}^{a,o}Q0,\bar{1}$	$9_{4,5;-1}$	$9_{4,6;-2}$	956.50	954.18	2.32	2.9646	71.0
${}^{a,o}Q0,\bar{1}$	$1_{1,0;1}$	$1_{1,1;0}$	32.44	29.76	2.68	1.5000	4870
${}^{a,o}Q0,\bar{1}$	$4_{2,2;0}$	$4_{2,3;-1}$	221.62	216.77	4.85	1.6472	6880
${}^{a,e}P2,\bar{3}$	$4_{2,2;0}$	$5_{0,5;-5}$	221.62	221.13	0.49	.0250	1.04
${}^{a,e}P2,\bar{3}$	$6_{2,4;-2}$	$7_{0,7;-7}$	403.23	401.92	1.31	.0115	1.39
${}^{a,e}R\bar{2},3$	$6_{0,6;-6}$	$5_{2,3;-1}$	305.27	303.70	1.57	.0178	5.05
${}^{a,e}R\bar{2},3$	$7_{1,6;-5}$	$6_{3,3;0}$	472.95	470.40	2.55	.0590	19.2
${}^{b,e}R\bar{1},3$	$7_{1,7;-6}$	$6_{2,4;-2}$	403.25	403.23	0.02	.1339	0.026
${}^{b,e}R\bar{1},3$	$7_{3,5;-2}$	$6_{4,2;2}$	577.63	577.07	0.56	.4666	30.3
${}^{b,o}P1,\bar{3}$	$3_{2,1;1}$	$4_{1,4;-3}$	156.98	155.85	1.13	.2156	468
${}^{b,e}R\bar{1},3$	$9_{4,6;-2}$	$8_{5,3;2}$	954.18	951.50	2.68	.6271	143
${}^{b,o}P1,\bar{3}$	$4_{3,1;2}$	$5_{2,4;-2}$	296.34	293.21	3.13	.2988	250
${}^{b,e}R\bar{1},3$	$5_{1,5;-4}$	$4_{2,2;0}$	225.12	221.62	3.50	.2226	3330
${}^{b,e}R\bar{1},3$	$6_{1,6;-5}$	$5_{2,3;-1}$	307.64	303.70	3.94	.1791	2250
${}^{b,e}R\bar{1},3$	$11_{5,7;-2}$	$10_{6,4;2}$	1423.60	1419.61	3.99	.8036	39.2
${}^{b,o}R\bar{1},1$	$11_{5,6;-1}$	$10_{6,5;1}$	1424.54	1419.59	4.95	.6841	51.3
${}^{b,o}R\bar{1},1$	$9_{4,5;-1}$	$8_{5,4;1}$	956.50	951.45	5.05	.5579	452
			(*D*) H_2S[b]				
${}^{b,e}P3,\bar{3}$	$3_{3,1;2}$	$4_{0,4;-4}$	115.68	114.15	1.53	.0013	0.74
${}^{b,o}R\bar{3},3$	$10_{2,8;-6}$	$9_{5,5;0}$	746.69[c]	744.65[c]	2.04	.0047	0.21
${}^{b,o}P3,\bar{5}$	$6_{6,0;6}$	$7_{3,5;-2}$	418.43	416.21	2.22	.0004	0.10
${}^{b,o}R\bar{3},3$	$7_{1,6;-5}$	$6_{4,3;1}$	362.59	360.29	2.30	.0034	3.8
${}^{b,e}R\bar{1},3$	$10_{3,8;-5}$	$9_{4,5;-1}$	746.69[c]	744.30[c]	2.39	.0047	0.84
${}^{b,e}R\bar{3},5$	$9_{4,6;-2}$	$8_{7,1;6}$	687.86	684.32	3.54	.0009	0.16
${}^{b,o}P1,\bar{3}$	$4_{2,2;0}$	$5_{1,5;-4}$	170.76	166.26	4.50	.0014	5.3
${}^{b,e}R\bar{1},3$	$7_{2,6;-4}$	$6_{3,3;0}$	362.59	357.37	5.22	.0035	6.9
${}^{b,e}Q1,\bar{1}$	$1_{1,0;1}$	$1_{0,1;-1}$	19.43	13.76	5.67	1.5000	58,330
${}^{b,o}P1,\bar{3}$	$7_{3,4;-1}$	$8_{2,7;-5}$	459.00	452.69	6.31	.0026	14
${}^{b,e}R\bar{3},5$	$11_{5,7;-2}$	$10_{8,2;6}$	1032.34[c]	1025.45[c]	6.89	.0011	0.13
${}^{b,e}R\bar{1},3$	$4_{1,4;-3}$	$3_{2,1;1}$	114.15	107.65	6.50	.0032	102
${}^{b,e}Q1,\bar{1}$	$2_{2,0;2}$	$2_{1,1;0}$	58.54	51.26	7.28	2.1289	37,710
${}^{b,e}P3,\bar{3}$	$7_{4,4;0}$	$8_{1,7;-6}$	459.74	452.69	7.05	.0026	5.8
${}^{b,e}P3,\bar{3}$	$4_{3,2;1}$	$5_{0,5;-5}$	174.39	166.26	8.13	.0012	45
${}^{b,o}P1,\bar{3}$	$10_{4,6;-2}$	$11_{3,9;-6}$	883.70[c]	875.36[c]	8.34	.0038	1.4
${}^{b,e}P3,\bar{3}$	$10_{5,6;-1}$	$11_{2,9;-7}$	883.75[c]	875.36[c]	8.39	.0038	4.4
${}^{b,o}R\bar{3},3$	$6_{1,5;-4}$	$5_{4,2;2}$	281.86	271.85	10.01	.0044	49
${}^{b,e}Q1,\bar{1}$	$3_{3,0;3}$	$3_{2,1;1}$	117.75	107.65	10.10	2.3196	179,000
${}^{b,e}R\bar{3},5$	$8_{4,5;-1}$	$7_{7,0;7}$	569.10	559.35	10.75	.0006	5
			(*E*) H_2Se[d]				
${}^{b,o}P3,\bar{5}$	$9_{8,1;7}$	$10_{5,6;-1}$	726.40	725.47	0.93	0.0014	0.012
${}^{b,o}P3,\bar{5}$	$10_{8,2;6}$	$11_{5,7;-2}$	848.92	847.93	0.99	0.0017	0.003
${}^{b,o}P1,\bar{3}$	$4_{2,2;0}$	$5_{1,5;-4}$	138.78	137.21	1.57	0.0035	0.57
${}^{b,o}R\bar{3},3$	$7_{1,6;-5}$	$6_{4,3;1}$	299.17	297.58	1.59	0.0100	2.3
${}^{b,e}P3,\bar{3}$	$11_{11,1;10}$	$12_{8,4;4}$	1142.86	1140.99	1.87	0.0004	0.000
${}^{b,e}R\bar{3},5$	$11_{6,6;0}$	$10_{9,1;8}$	898.33	895.55	2.78	0.0015	0.017
${}^{b,o}P1,\bar{3}$	$7_{3,4;-1}$	$8_{2,7;-5}$	376.78	373.75	3.03	0.0030	1.7
${}^{b,o}R\bar{3},3$	$10_{2,8;-6}$	$9_{5,5;0}$	614.66	611.11	3.55	0.0100	0.78
${}^{b,e}P3,\bar{3}$	$3_{3,1;2}$	$4_{0,4;-4}$	97.80	94.14	3.66	0.0028	3.1
${}^{b,e}R\bar{3},5$	$12_{7,6;1}$	$11_{10,1;9}$	1086.64	1082.52	4.12	0.0015	0.044
${}^{b,o}P1,\bar{3}$	$10_{4,6;-2}$	$11_{3,9;-6}$	724.95	720.77	4.18	0.0087	0.55
${}^{b,e}P3,\bar{3}$	$10_{5,6;-1}$	$11_{2,9;-7}$	725.47	720.77	4.70	0.0084	2.0
${}^{b,e}Q1,\bar{1}$	$1_{1,0;1}$	$1_{0,1;-1}$	16.09	11.08	5.01	1.5000	14,000

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[a] The lines with predicted values of $\nu=0$ will have $\alpha=0$. The values tabulated in parentheses are α/ν^2. If the lines occur at a finite frequency (as theoretically they will because the splitting is finite although small, and perturbations may increase it substantially), the absorption coefficient can be obtained by multiplying the tabulated value by ν^2.

[b] The line strengths given for H_2S are those for $\kappa=0.5$, since these do not differ appreciably from the interpolated strengths for the actual value of $\kappa=0.523$.

[c] Rigid rotor energy values.

[d] The line strengths given for H_2Se are those for $\kappa=0.3$, since these do not differ appreciably from the interpolated strengths for the actual value of $\kappa=0.315$.

TABLE III. Exact values of the reduced energy, $E(\kappa)$, for H_2O, $\kappa = -0.436426$.

$J_{K_{-1}, K_1; \tau}$	$E(\kappa)$	$J_{K_{-1}, K_1; \tau}$	$E(\kappa)$
$0_{0,0;0}$	0.00000	$5_{5,0;5}$	21.54000
$1_{1,0;1}$	0.56357	$5_{5,1;4}$	21.53968
$1_{1,1;0}$	0.00000	$5_{4,1;3}$	6.37690
$1_{0,1;-1}$	−1.43643	$5_{4,2;2}$	6.35287
$2_{2,0;2}$	2.69953	$5_{3,2;1}$	−4.96391
$2_{2,1;1}$	2.56357	$5_{3,3;0}$	−5.49647
$2_{1,1;0}$	−1.74570	$5_{2,3;-1}$	−11.75282
$2_{1,2;-1}$	−3.43643	$5_{2,4;-2}$	−15.08139
$2_{0,2;-2}$	−4.44523	$5_{1,4;-3}$	−16.85100
$3_{3,0;3}$	6.94336	$5_{1,5;-4}$	−24.77173
$3_{3,1;2}$	6.92214	$5_{0,5;-5}$	−24.89899
$3_{2,1;1}$	−1.11110	$6_{6,0;6}$	31.84431
$3_{2,2;0}$	−1.74570	$6_{6,1;5}$	31.84428
$3_{1,2;-1}$	−5.30762	$6_{5,1;4}$	13.27250
$3_{1,3;-2}$	−8.66784	$6_{5,2;3}$	13.26907
$3_{0,3;-3}$	−9.25316	$6_{4,2;2}$	−1.71566
$4_{4,0;4}$	13.23716	$6_{4,3;1}$	−1.83091
$4_{4,1;3}$	13.23443	$6_{3,3;0}$	−12.39928
$4_{3,1;2}$	1.53971	$6_{3,4;-1}$	−13.80339
$4_{3,2;1}$	1.39636	$6_{2,4;-2}$	−18.77578
$4_{2,2;0}$	−5.91631	$6_{2,5;-3}$	−24.28828
$4_{2,3;-1}$	−7.59867	$6_{1,5;-4}$	−25.31308
$4_{1,3;-2}$	−10.26823	$6_{1,6;-5}$	−35.74059
$4_{1,4;-3}$	−15.76062	$6_{0,6;-6}$	−35.79273
$4_{0,4;-4}$	−16.04937		

this was discovered as absorption of radar waves. This line, $6_{1,6} - 5_{2,3}$, has been observed experimentally.[10, 11, 12]

The observed position of 0.7418 cm^{-1} differs considerably (from the microwave point of view) from the value of 0.78 cm^{-1} predicted from term values, but from inspection of Table II, there can be no doubt that on the basis of position alone this is the correct identification.

The identification is substantiated by the observed intensity. The calculation of the microwave absorption of water vapor and the comparison with experiment are discussed in detail in reference 1. In order to illustrate the use of Table II we can briefly summarize the comparison of calculated and observed absorption coefficients at resonance as follows. The calculated absorption coefficient value (for 14.5°C) at the predicted position of 0.78 cm^{-1} and round value of $\Delta\nu_0 = 0.1$ cm^{-1} is 37.8×10^{-6} cm^{-1}. When corrected for the observed position[12] and observed half-width[7] of 0.087 cm^{-1}, the absorption coefficient for water vapor in air, at a concentration of 1 g/m^3 and 14.5°C is 0.049×10^{-6} cm^{-1}. At 45°C the coefficient is 0.0522×10^{-6} cm^{-1}, which is in good agreement with the observed[7] absorption coefficient of 0.0573×10^{-6} cm^{-1}.

The theoretical value for pure water vapor is the tabulated value, corrected for position, and for the observed half-width of 0.36 cm^{-1}, namely 9.6×10^{-6} cm^{-1}. This agrees with the observed[12] value of $8 \pm 4 \times 10^{-6}$ cm^{-1}.

D_2O

The microwave absorption of D_2O should be as interesting as that of H_2O. On account of the heavier atoms and resulting larger moments of inertia, a few more lines appear in the region. However, the increase in the moments of inertia makes the partition function larger, so that each level has a smaller population. The intensities of the lines are on the average smaller.

The term values of D_2O are known,[13] and the possible transitions in the microwave region (above 0.2 cm) are listed in Table II. The line strengths were obtained by interpolating the basic table[4] in the light of Table I. The dipole moment of D_2O will be very nearly the same as for H_2O. The mean free time will be the same except for a small mass correction, which, according to the simple kinetic theory derivation, makes $\Delta\nu$ for D_2O 0.95 as large as for H_2O. Thus the intensities of the D_2O lines relative to the H_2O lines are quite accurately calculated. Only weak lines are predicted near 1 cm and none have been observed in the region studied[12] (0.73 to 0.89 cm^{-1}).

HDO

Besides having moments of inertia intermediate between H_2O and D_2O, and thus giving rise to a similar selection of lines in the microwave region, HDO is of particular importance because its

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[10] R. L. Kyhl, R. H. Dicke, and R. Beringer, Phys. Rev. **69**, 694 (1946), estimated the position at 1.34 cm. See also R. H. Dicke, R. Beringer, R. L. Kyhl and A. B. Vane, Phys. Rev. **70**, 340 (1946).

[11] S. H. Autler, G. E. Becker, and J. M. B. Kellogg, Phys. Rev. **69**, 694 (1946), give 22,320±150 megacycles, or 1.33 cm, or 0.744 cm^{-1}, and the attenuation as 0.044 db/nautical mile for 1 g water vapor per cubic meter. In reference 7 they give the attenuation data in more detail. At 0.751 cm^{-1} it is 0.0249 db/km per g/cu. m.

[12] C. H. Townes and F. R. Merritt, Phys. Rev. **70**, 558 (1946), give 22,237±5 megacycles or 0.7418 cm^{-1}, and intensity as $4 \pm 2 \times 10^{-6}$ nepers/cm.

[13] N. Fuson, H. M. Randall, and D. M. Dennison, Phys. Rev. **56**, 982 (1939).

permanent dipole has components along two axes of inertia. Thus, in addition to the lines of the type where the dipole is parallel only to the axis of the intermediate moment of inertia (b-type) permitted in H_2O and D_2O, there will be lines from transitions permitted when the dipole has a component along the axis of the smallest moment of inertia (a-type). The values of the dipole moments, to be substituted in (1), will be that of H_2O multiplied by $\cos^2\theta$ for the b-type and $\sin^2\theta$ for the a-type, θ being 20° 38′.

The levels of the asymmetric rotor are characterized by the fact that they are split from doubly degenerate symmetric-rotor levels. The amount of splitting depends on the degree of asymmetry, κ. For HDO κ is -0.7, so that the degenerate levels of the prolate symmetric rotor are split, and levels of the same K_{-1} index will be paired, the separation being very small at high K_{-1} values. But it is between exactly these levels that the a-type transitions occur. It is seen then that absorption lines will occur throughout the microwave and radio regions for such a-type transitions.

The expected transitions are listed in Table II*C* with position and intensity. It is felt that the intensities are calculable with sufficient accuracy. The position depends on estimates of the rotational energy levels of HDO. There are no term values known for this molecule. The only completely resolved spectrum of HDO is the one at 1.1μ which has been measured and analyzed by L. Herzberg.[14] We have reanalyzed this spectrum on the basis of the asymmetric-rotor intensities and found that the effective moments given by Herzberg are satisfactory. With these one can

TABLE IV. The Hamiltonian is a direct sum of blocks of order $2J+1$ belonging to each value of the quantum number J By the symmetry of the Four Group these blocks can be divided into four submatrices, one for each representation. These are labelled ee, eo, oe, oo, where e, o in the first and second indices refer respectively to the parity of K_{-1} and K_1 which are the absolute values of the internal quantum numbers of the limiting cases of prolate and oblate symmetric rotors. Each state of the asymmetric rotor, $A(J, (K_{-1}, K_1), M, \gamma)$ is identified by the absolute values of the inner quantum numbers (K_{-1}, K_1) it would have in these two limiting cases. This state is a linear combination of Wang functions.

$$A(J, (K_{-1}, K_1), M, \gamma)=\Sigma_K t, {}_{K(K_{-1}, K_1)}S(J, K, M, \gamma). \tag{3}$$

Thus, the columns of the matrices $T=||t_{ij}||$ in the table refer to asymmetric state, identified by K_{-1}, K_1 (at the head of the columns). The Wang functions $S(J, K, M, \gamma)$ from which the asymmetric states are constructed are identified by the absolute magnitudes of the quantum number K, and γ which describes whether + or − combinations of the symmetric-rotor states were taken. The values of K and γ are indicated in the table on each row of the matrices.

The Hamiltonian diagonalized by these matrices T is of Type II^r, which refers to the fact that the Wang functions used as basis functions are those with symmetry axis parallel to the intermediate axis of inertia. Thus the K's are neither K_{-1} nor K_1 (indeed they may have opposite parity), for the latter refer to inner quantum numbers of Wang functions of symmetry along the least and greatest axes of inertia, respectively. The summation over K in (3) is then over the values listed explicitly on the rows of the submatrices displayed.

2ee

	20	02
0^+	.78878	.61468
2^+	.61468	−.78878

3eo

	21	03
1^-	.58817	.80873
3^-	.80873	−.58817

3oe

	30	12
1^+	.94200	.33560
3^+	.33560	−.94200

3oo

	31	13
0^+	.74564	.66634
2^+	.66634	−.74564

4eo

	41	23
1^+	.90763	.41976
3^+	.41976	−.90763

4oe

	32	14
1^-	.55707	.83047
3^-	.83047	−.55707

4oo

	31	13
2^-	.84957	.52748
4^-	.52748	−.84957

5ee

	42	24
2^-	.78878	.61468
4^-	.61468	−.78878

4ee

	40	22	04
0^+	.70012	.40889	.58536
2^+	.69076	−.18031	−.70024
4^+	.18077	−.89459	.40868

5eo

	41	23	05
1^-	.48457	.40145	.77719
3^-	.81551	.11409	−.56739
5^-	.31644	−.90875	.27210

5oe

	50	32	14
1^+	.87636	.40298	.26384
3^+	.47169	−.60712	−.63947
5^+	.09751	−.68485	.72212

5oo

	51	33	15
0^+	.66647	.46684	.58127
2^+	.70048	−.12521	−.70260
4^+	.25523	−.87543	.41046

6eo

	61	43	25
1^+	.84960	.43932	.29185
3^+	.50513	−.51853	−.68991
5^+	.15176	−.73357	.66245

6oe

	52	34	16
1^-	.43478	.47930	.76239
3^-	.79528	.19282	−.57476
5^-	.42248	−.85621	.29734

6oo

	51	33	15
2^-	.72529	.50319	.46985
4^-	.66290	−.32625	−.67389
6^-	.18580	−.80023	.57018

6ee

	60	42	24	06
0^+	.63933	.44008	.30151	.55379
2^+	.70246	−.02605	−.19533	−.68391
4^+	.30830	−.77628	−.32937	.44029
6^+	.05267	−.45060	.87319	−.17813

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[14] L, Herzberg, Zeits. f. Physik **107**, 549 (1937).

compute the rotational energy levels assuming the molecule is a rigid rotor. The corrections to be applied to the rigid-rotor levels will be large, as in H_2O. However, in computing the positions of the microwave lines these corrections cancel to a large extent. For example, levels with same first subscript (K_{-1}) have about the same correction (as in the $5_{3,2}-5_{3,3}$ transition). All the *a*-type lines occur between levels of the same J and K_{-1}, so that the correction cancels in predicting these levels; that is the positions of these lines are given very closely by the splitting of the rigid-rotor levels. Fortunately, the same considerations also apply to the strongest *b*-type line; the correction for H_2O also cancels for the levels involved. On the other hand, the positions of the other *b*-lines are not known within one or more wave numbers, on account of expected deviations from rigid-rotor levels.

All the expected transitions lying at wavelengths longer than 0.2 cm are listed in Table II*C*. All the "split" levels ${}^{a,o}Q_{0,\bar{1}}$ are listed first, followed by the other *a*-type lines, and finally by the *b*-type lines. A line of HDO has been observed[12] at 0.7442 cm^{-1}. This is in close agreement with the predicted position of 0.79 cm^{-1} for transition $5_{3,2}-5_{3,3}$. The calculated absorption coefficient of this line is the tabulated value, adjusted for the observed position and half-width ($\Delta\nu_0=0.27$ cm^{-1}), namely 26.2×10^{-6} cm^{-1}. This is in good agreement with the observed intensity of $30\pm14\times10^{-6}$ cm^{-1}. Other lines given in Table II*C* would have approximately the observed intensity, if they appeared at the observed position. However, it seems unlikely that the predicted position would be in error by the amount required.

H_2S

On account of the increased mass of sulphur over oxygen atoms, the microwave spectrum of H_2S should be somewhat richer than H_2O, although the chance that a line will appear in any accessible region remains very small. Again term values are not known, but effective moments of inertia of the ground state have been found with considerable accuracy,[15] and a correction for centrifugal distortion applied. These calculated levels should be accurate to a few hundredths of a wave number, so that the positions given in Table II*D* are equally reliable. The intensities have been calculated as above. The value used for the dipole moment was 1.10×10^{-18} esu-cm.

Several lines between 0.1 and 1.0 cm are very strong, although this is in part due to the ν^2 term. The absorption of H_2S has been measured[16] at two frequencies, 0.31 and 0.81 cm^{-1}. The absorption coefficient (for 1 atm.) was reported as ~ 0 and $\sim 30\times10^{-6}$ cm^{-1}, respectively. Absorption by H_2S at this wave-length would probably be due to the wings of the intense lines at 5.67, 7.28 and 10.10 cm^{-1}, which can be calculated by the shape factor given by Van Vleck and Weisskopf, Eq. (19) of reference 1. If $\Delta\nu_0$ were 0.1 cm^{-1}, the total contribution would only be 1×10^{-6} cm^{-1}. Further investigation of the absorption of H_2S in this region would be of value to estimate the value of $\Delta\nu_0$ for comparison with that of H_2O.

HDS AND D_2S

Infra-red bands of these molecules have not been analyzed so that neither term values nor effective moments of inertia are known. Furthermore, it is not yet possible to estimate the moments of inertia of HDS and D_2S accurately enough by allowing for the increased mass of deuterium, because the effective moments depend on the vibrational quantum number, and hence on the half quantum numbers of the ground state. This introduces a substantial correction which can only be estimated by the isotope effect on the coefficients showing the dependence of the moments of H_2S on vibrational quantum numbers, which is not yet known. Qualitatively, the microwave region spectrum of these molecules will be similar to those of HDO and D_2O, being somewhat richer in lines on account of the increased mass of the central atom.

The spectrum of HDS, like that of HDO, should be composed of both *a*- and *b*-type lines, and should extend throughout the microwave and radio regions.

H_2Se

The H_2Se molecule is similar in shape to that of H_2O and H_2S, and will have the same kind of

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[15] B. L. Crawford and P. C. Cross, J. Chem. Phys. **5**, 621 (1937).

[16] J. E. Walter and W. D. Hershberger, J. App. Phys. **17**, 814 (1946).

microwave absorption spectrum. We have made an analysis of the infra-red band[17] of H_2Se at 4.3μ and find the effective moments of inertia are in the neighborhood of $I_A=3.14$, $I_B=3.89$, $I_C=7.18\times10^{-40}$ g cm^2.

These values were substituted in the formulae for the rigid rotor and the positions of the transitions in the microwave region (0.2 cm and longer) calculated as shown in Table II*E*. These positions are only approximate, but indicate that one line might be detectable in the one-centimeter region.

The dipole moment of H_2Se is not known. A guess of 0.7×10^{-18} esu-cm was used in estimating the order of magnitude of the absorption coefficient. If the $7_{1,6}-6_{4,3}$ line can be detected, its intensity will serve to determine the dipole moment.

The spectrum of HDSe will be of considerable interest in relation to those of HDO and HDS.

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The authors are pleased to express their appreciation of the interest and helpful advice of Professor J. H. Van Vleck in the preparation of this material.

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[17] D. M. Cameron, W. C. Sears, and H. H. Nielsen, J. Chem. Phys. **7**, 994 (1939).

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Note on the Spherical Harmonic Method As Applied to the Milne Problem for a Sphere*

R. E. MARSHAK
University of Rochester, Rochester, New York

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The spherical analog of the Milne problem for the half-plane is treated by an approximate method based on expanding the neutron distribution function in a finite number of spherical harmonics. The results are improved markedly in going from the first to the second approximation and more slowly in higher approximations. The neutron distribution is calculated in the first two approximations. Values of the "extrapolated endpoint"—as predicted by the first three approximations—are tabulated in Table I as a function of the radius of the sphere.

1.

We consider the following problem: a black sphere of radius a, i.e., a sphere which absorbs completely all neutrons which fall upon it, is surrounded by an infinite non-capturing medium which scatters neutrons isotropically without changing their velocity. No sources are present in the outer medium except that a current density of amount $(F/4\pi r^2)$ (F is a constant) is assumed to exist in the direction $(-r)$. We wish to determine the neutron density in the (outer) medium.[1]

This problem is the complete analog of the Milne problem for the semi-infinite plane since the albedo of the black core is zero just as the albedo of vacuum is zero in the plane case. If the black core is replaced by vacuum, the albedo is no longer zero, and the physical conditions are altered in an essential way. The modified problem is not treated in this note.

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* The contents of this note were published in a Montreal Report (MT-49) dated April 15, 1944. The Central Records File Reference giving authority for declassification is 11-5-3, serial No. 47. The spherical harmonic method has been generalized and applied to a great variety of neutron diffusion problems by C. Mark (declassified Montreal report MT-97), B. Carlson (declassified Los Alamos report LADC No. 108), R. Glauber, and W. Rarita. Another approximation method based on the Gauss formula for numerical integration, which is equivalent in certain ways to the spherical harmonic method (cf. footnotes below), was developed independently by G. C. Wick, Zeits. f. Physik **121**, 702 (1943), and applied to problems of the stellar atmosphere by S. Chandrasekhar, Astrophys. J. **100**, 76 (1944) and succeeding papers. Because of the war, Wick's paper did not come to the attention of the author until the present work was completed.

[1] S. Chandrasekhar, Astrophys. J. **101**, 95 (1945) has worked out the converse of this problem, namely the determination of the distribution function due to a point source in a spherical scattering medium surrounded by vacuum, by Wick's method.