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Theory of the Effect of Temperature on the Electron Diffraction Patterns of Diatomic Molecules* †

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The effect of temperature on the electron diffraction pattern of a diatomic molecule is considered from the standpoint of the simple kinematic scattering theory utilizing a quartic vibrational potential. The potential is obtained by an expansion of $\hbar^2 J(J+1)/2\mu r^2 + D \exp[-2a(r-r_e)]-2D \exp[-a(r-r_e)]$ about its minimum value r_0. The second-order wavefunction for the nth vibrational and Jth rotational state of the system has been obtained, and expressions for the electron diffraction quantities r_g, l_e^2, and $M(s)$ have been computed. General results for the quantity $M(s)$ utilizing the approximate eigenfunctions of the complete Morse potential and incorporating an approximate treatment of the effect of centrifugal stretching are also presented. Explicit expressions for $M(s)$ for the first three vibrational states as derived by this treatment are given. Appropriate sums over all the vibrational and rotational states have been carried out to obtain the temperature dependence for the above quantities. Estimates of the effect of temperature on the parameters r_g and l_e^2 at 300° and 1500°K for representative diatomic molecules are given.

A NUMBER of authors have considered the effects of anharmonic molecular vibrations on electron diffraction results.[1-4] Approximate corrections for the effects of centrifugal stretching have also been considered by Bartell[1] and Iwasaki and Hedberg.[3] However, a detailed general treatment of the effects of temperature on the electron diffraction parameters r_g, l_e^2, and the $M(s)$ function, for cases where one or more excited vibrational states make an important contribution to the scattering, has not been treated either for the diatomic or polyatomic cases. It is the purpose of this paper to outline two general solutions to this problem for the case of diatomic molecules.

PERTURBED HARMONIC OSCILLATOR APPROXIMATION

For the case of a diatomic molecule, the complete quantum-mechanical description of the system in the center of mass coordinates may be approximately separated into a rotational and vibrational part and an electronic part.[5] Further separation of the rotational–vibrational problem can be accomplished by using the rigid rotor as an approximation for the rotational problem.[6]

This then reduces the vibrational problem to a solution of the radial equation

$$(d^2/dr^2)Q_n(r) + [E_n - W(r)]Q_n(r) = 0 \qquad (1.0)$$

for the vibrational eigenfunctions $Q_n(r)$. Here, $W(r)$ is $(2\mu/\hbar^2)V(r) + J(J+1)/r^2$, where μ is the reduced mass for the molecule and $V(r)$ is the vibrational potential function. The separation term $J(J+1)/r^2$ is commonly referred to as the centrifugal stretching

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[1] L. S. Bartell, J. Chem. Phys. **23**, 1219 (1955).

[2] K. Kuchitsu and L. S. Bartell, J. Chem. Phys. **35**, 1945 (1961).

[3] K. Hedberg and M. Iwasaki, J. Chem. Phys. **36**, 589 (1962).

[4] A. Reitan, Acta Chem. Scand. **12**, 131 (1958).

[5] M. Born and E. Oppenheimer, Ann. Physik **84**, 457 (1927).

[6] See for instance, H. Eyring, J. Walter and G. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1954), p. 268.

term. The energy E_n is, of course, $2\mu/\hbar^2$ times the true vibrational energy ϵ_n.

For our purposes, it will be convenient to define a new variable z such that

$$z = B^{\frac{1}{2}}(r - r_0), \quad (1.1)$$

where B is a constant given by

$$B = [\tfrac{1}{2}W^{\mathrm{II}}(r_0)]^{\frac{1}{2}}, \quad (1.2)$$

where the Roman numeral two signifies the second derivative of the function, $W(r)$. r_0 is the minimum of $W(r)$ given as

$$r_0 \cong r_e + 4l_\alpha{}^4 J(J+1)/r_e{}^3, \quad (1.3)$$

where r_e is the minimum of $V(r)$ and l_α is given by the relation $l_\alpha{}^2 = \hbar/[2a(2\mu D)^{\frac{1}{2}}]$ where a is the anharmonicity constant appearing in the Morse function, μ is the rest mass of the molecule, and D is the dissociation energy of the molecule. The function $W(r)$ can then be expanded about its minimum r_0 in a Taylor series.[7] In this treatment, the Morse potential,[8] which is sufficiently accurate for our purposes,[2] is used for $V(r)$. This results in the series

$$W(r) \cong W(r_0) + Bz^2 + Cz^3 + Dz^4 + \cdots, \quad (1.4)$$

where C and D are given as

$$C = [\tfrac{1}{6}W^{\mathrm{III}}(r_0)][\tfrac{1}{2}W^{\mathrm{II}}(r_0)]^{-3/4}, \quad (1.5)$$

and

$$D = [\tfrac{1}{24}W^{\mathrm{IV}}(r_0)][\tfrac{1}{2}W^{\mathrm{II}}(r_0)]^{-1}. \quad (1.6)$$

The unperturbed Hamiltonian is then

$$H_0 = B[(d/dz)^2 - z^2], \quad (1.7)$$

with normalized eigenfunctions

$$Q_n{}^{(0)}(z) = (2^n n!)^{-\frac{1}{2}}(B/\pi)^{\frac{1}{4}}H_n(z)\exp[-\tfrac{1}{2}z^2], \quad (1.8)$$

and eigenvalues

$$E_n{}^{(0)} = W(r_0) + B(2n+1). \quad (1.9)$$

Using second-order time-independent perturbation theory,[9] the wavefunction which will give results for r_g and $l_e{}^2$ correct through terms in C^3 and CD was found to be

$$Q_n{}^{(2)}(z) = A_n Q_n{}^{(0)}(z) + A_{n+1}Q_{n+1}{}^{(0)}(z) + A_{n-1}Q_{n-1}{}^{(0)}(z)$$
$$+ A_{n+2}Q_{n+2}{}^{(0)}(z) + A_{n-2}Q_{n-2}{}^{(0)}(z) + A_{n+3}Q_{n+3}{}^{(0)}(z)$$
$$+ A_{n-3}Q_{n-3}{}^{(0)}(z) + A_{n+4}Q_{n+4}{}^{(0)}(z) + A_{n-4}Q_{n-4}{}^{(0)}(z), \quad (1.10)$$

where

$$A_n = 1 - C^2(87 + 256n + 246n^2 + 164n^3)/(576B^2), \quad (1.11)$$

$$A_{n+1} \cong [C(2n+2)^{\frac{1}{2}}/(16B)]$$
$$\times \{-6(n+1) + D(392 + 646n + 317n^2 - 27n^3)/(16B)\}, \quad (1.12)$$

$$A_{n-1} = [C(2n)^{\frac{1}{2}}/(16B)]$$
$$\times [6n - D(90 + 69n + 398n^2 + 27n^3)/(16B)], \quad (1.13)$$

$$A_{n+2} = \{[(n+1)(n+2)]^{\frac{1}{2}}/(8B)\}$$
$$\times [-D(2n+3) + C^2(27 + 33n + 7n^2)/(8B)], \quad (1.14)$$

$$A_{n-2} = \{[n(n-1)]^{\frac{1}{2}}/(8B)\}$$
$$\times [D(2n-1) + C^2(1 - 19n + 7n^2)/(8B)], \quad (1.15)$$

$$A_{n+3} = -[\tfrac{1}{2}(n+1)(n+2)(n+3)]^{\frac{1}{2}}[C/(12B)], \quad (1.16)$$

$$A_{n-3} = [\tfrac{1}{2}n(n-1)(n-2)]^{\frac{1}{2}}[C/(12B)], \quad (1.17)$$

$$A_{n+4} = \{[(n+1)(n+2)(n+3)(n+4)]^{\frac{1}{2}}/(32B)\}$$
$$\times [-D + C^2(4n+7)/(4B)], \quad (1.18)$$

and

$$A_{n-4} = \{[n(n-1)(n-2)(n-3)]^{\frac{1}{2}}/(32B)\}$$
$$\times [D + C^2(4n-3)/(4B)]. \quad (1.19)$$

With this wavefunction, expressions were obtained for r_g, defined by the relation[2]

$$r_g = r_0 + B^{-\frac{1}{2}}\int_{-\infty}^{\infty} dz\, z\, P(z) \quad (1.20)$$

and $l_e{}^2$ defined as[2]

$$l_e{}^2 = B^{-1}\int_{-\infty}^{\infty} dz\, z^2 P(z) + 2(r_g - r_0)(r_0 - r_e) + (r_0 - r_e)^2, \quad (1.21)$$

where $P(z)$ is simply the square of $Q_n{}^{(2)}(z)$. It should be noted that to first-order terms, the first term in (1.21) is $l_e{}^2$ for a nonrotating molecule, the second term is a rotation–vibration coupling term, and the last is the effect of rotation on $l_e{}^2$.[10] With the wavefunction given by (1.10), the results for r_g and $l_e{}^2$, containing only terms in the first power of $J(J+1)$, are

$$r_g \cong r_e + 3al_\alpha{}^2\tfrac{1}{2}(2n+1) - a^3l_\alpha{}^4$$
$$\times \tfrac{1}{192}(1091 + 2282n + 1675n^2 - 1214n^3 - 607n^4)$$
$$+ 4l_\alpha{}^4 J(J+1)/r_e{}^3 + l_\alpha{}^6(13a^2 - 27a/r_e + 24/r_e{}^2)$$
$$\times (2n+1)J(J+1)/r_e{}^3$$
$$- l_\alpha{}^8(95a^4 - 189a^3/r_e + 84a^2/r_e{}^2 + 180a/r_e{}^3)$$
$$\times (31 + 78n + 78n^2)J(J+1)/(18r_e{}^3)$$
$$+ l_\alpha{}^8(5a^4 - 12a^3/r_e + 12a^2/r_e{}^2)$$
$$\times (645 + 2086n + 2693n^2 + 1214n^3 + 607n^4)$$
$$\times J(J+1)/(48r_e{}^3) \quad (1.22)$$

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[7] This treatment is similar to that outlined in L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), p. 305.

[8] P. M. Morse, Phys. Rev. **34**, 57 (1929).

[9] See reference 7, page 154.

[10] The authors are indebted to L. S. Bartell for pointing out the physical significance of the terms in (1.21).

and

$$l_e^2 \simeq l_\alpha^2(2n+1)+a^2l_\alpha^4 \tfrac{1}{4}(15+46n+46n^2)$$

$$+6l_\alpha^6(3a-1/r_e)(2n+1)J(J+1)/r_e^3$$

$$-a^3l_\alpha^8(1091+2282n+1675n^2-1214n^3-607n^4)$$

$$\times J(J+1)/(24r_e^3)+l_\alpha^8(26a^3-54a^2/r_e+48a/r_e^2)$$

$$\times(11+30n+30n^2)J(J+1)/(3r_e^3)$$

$$-l_\alpha^8(27a^3-42a^2/r_e+60/r_e^3)$$

$$\times(1+2n+2n^2)J(J+1)/r_e^3. \quad (1.23)$$

The temperature dependence of (1.22) and (1.23) can then be obtained by summing over all the vibrational and rotational states, which results in the expressions

$$r_g \simeq r_e+3al_\alpha^2 \tfrac{1}{2}\coth(hv/2kT)$$

$$+a^3l_\alpha^4 \tfrac{1}{384}[707-4710 \coth^2(hv/2kT)$$

$$+1821 \coth^4(hv/2kT)]$$

$$+4l_\alpha^4 \cot[\hbar/(2IkT)^{\frac{1}{2}}]/[r_e^3\hbar/(2IkT)^{\frac{1}{2}}]$$

$$+l_\alpha^6(13a^2-27a/r_e+24/r_e^2) \coth(hv/2kT)$$

$$\times\cot[\hbar/(2IkT)^{\frac{1}{2}}]/[r_e^3\hbar/(2IkT)^{\frac{1}{2}}], \quad (1.24)$$

and

$$l_e^2 \simeq l_\alpha^2 \coth(hv/2kT)+a^2l_\alpha^4 \tfrac{1}{4}[23 \coth^2(hv/2kT)-8]$$

$$+6l_\alpha^6(3a-1/r_e)[\coth(hv/2kT)]$$

$$\times\cot[\hbar/(2IkT)^{\frac{1}{2}}]/[r_e^3\hbar/(2IkT)^{\frac{1}{2}}]$$

$$+a^3l_\alpha^8[707-4710 \coth^2(hv/2kT)$$

$$+1821[\coth^4(hv/2kT)]$$

$$\times\cot[\hbar/(2IkT)^{\frac{1}{2}}]/[48r_e^3\hbar/(2IkT)^{\frac{1}{2}}]$$

$$-l_\alpha^8(27a^3-42a^2/r_e+60/r_e^3)[\coth^2(hv/2kT)]$$

$$\times\cot[\hbar/(2IkT)^{\frac{1}{2}}]/[r_e^3\hbar/(2IkT)^{\frac{1}{2}}]$$

$$+l_\alpha^8(26a^3-54a^2/r_e+48a/r_e^2)[15 \coth^2(hv/2kT)-4]$$

$$\times\cot[\hbar/(2IkT)^{\frac{1}{2}}]/[3r_e^3\hbar/(2IkT)^{\frac{1}{2}}]. \quad (1.25)$$

In obtaining the above averages, the energy terms proportional to $(2n+1)^2$, $(2n+1)J(J+1)$, and $[J(J+1)]^2$ were neglected in the Boltzman weighting factor and equilibrium frequencies were used in the calculations. It can be easily shown that the neglect of these terms will introduce an error of less than 15% in the normalization in the worst case considered by this work. Since the correction terms are both multiplied and divided by the normalization factor in the computation of the averages, the error in the corrections given by (1.24) and (1.25) should be accurate to better than 15% at 1500°K for the worst case considered. There is, of course, the possibility that contributions of the order of C^4, C^2D, and D^2 from the

third-order wavefunction will make an important contribution at high temperatures.

In Tables I and II, the results for r_g and l_e are given for some selected diatomic molecules at 300° and 1500°K. In the case of the halogens, the correction terms proportional to C^3 give rise to extremely large corrections at 1500°K, and in fact, give an incorrect result for $T=0°$K so that the contributions from the third-order wavefunction mentioned previously should be considered for accurate work. The results for r_g indicate that at most temperatures the classical treatment of the centrifugal stretching effect given by Bartell[1] is adequate. However, at low temperatures for molecules with small moments of inertia, such as H_2, the term $\cot[\hbar/(2IkT)^{\frac{1}{2}}]/(\hbar/(2IkT)^{\frac{1}{2}})$ may differ appreciably from $2IkT/\hbar^2$, and the former expression is therefore a better approximation in these cases. In the calculation of l_e^2, the contribution of terms depending only on J are less than 1/10 000 of an angstrom unit for all the cases studied. The rotation–vibration coupling terms on the other hand make significant contributions—even at 300°K which in the case of O_2 amounts to about 0.0002 A. Some of the details of the rotational averaging are given in Appendix I.

It is also possible to calculate the effect of the anharmonicity and centrifugal stretching terms on the $M(s)$ function using the wavefunctions given in (1.10). Since this approach is rather cumbersome, it will be presented here only through terms in the first power of C, the cubic coefficient in the potential. A more detailed treatment of the effects of temperature on the $M(s)$ function is presented in a later part of this paper.

The $M(s)$ function calculated with a cubic potential and a first-order wavefunction is given as

$$M(s)=Kc(s)\sum_{n=0}^{\infty} \exp[-(hv/2kT)(2n+1)]$$

$$\times\sum_{J=0}^{\infty} \exp[-(\hbar^2/2IkT)J(J+1)]$$

$$\times\sum_{m=-J}^{J} \langle Y_J^m(\theta,\phi)Q_n^{(1)}(r,J) \mid \exp(is\cdot r)$$

$$\times \mid Y_J^m(\theta,\phi)Q_n^{(1)}(r,J)\rangle, \quad (1.26)$$

where $c(s)$ is a coefficient depending on the scattering of the individual atoms,[11] the $Y_J^m(\theta,\phi)$ are the normalized spherical harmonics which are the eigenfunctions of the rigid rotor Hamiltonian, the $Q_n^{(1)}(r,J)$ are the first-order vibrational wavefunctions for a cubic Morse oscillator and K is a normalization constant. Making use of the sum rule for spherical harmonics[12] and integrating over the angular coordinates, (1.26)

[11] See for instance, R. A. Bonham, and T. Ukaji, J. Chem. Phys. 36, 72 (1962).

[12] P. M. Morse and H. Feshbach, Methods of Theoretical Physics (McGraw-Hill Book Company, Inc., New York, 1953), Vol. II, p. 1327.

TABLE I. Vibrational, rotational, and vibrational-rotational coupling contributions to r_g at 300° and 1500°K for selected diatomic molecules.

	r_e	Vibrational contribution		Rotational contribution		Vibration-rotation coupling term		r_g	
		$T=300°K$	$T=1500°K$	$T=300°K$	$T=1500°K$	$T=300°K$	$T=1500°K$	$T=300°K$	$T=1500°K$
$H_2{}^1$	0.7417^a	0.020_2	0.020_8	0.001_9	0.010_6	0.000_1	0.000_4	0.763_9	0.773_5
H^1Cl^{35}	$1.274_6{}^a$	0.015_2	0.017_1	0.001_3	0.006_5	...	0.000_2	1.291_1	1.298_4
$N_2{}^{14}$	$1.097_6{}^a$	0.004_1	0.005_1	0.000_3	0.001_5	...	...	1.102_0	1.104_2
$N^{14}O^{16}$	$1.150_8{}^a$	0.004_7	0.006_7	0.000_5	0.002_3	...	...	1.156_0	1.159_8
$O_2{}^{16}$	$1.207_4{}^a$	0.005_9	0.009_3	0.000_7	0.003_4	...	0.000_1	1.214_0	1.220_2
$Cl_2{}^{35}$	$1.989_0{}^b$	0.005_1	0.039_2	0.001_3	0.006_4	...	0.000_3	1.995_4	2.034_9
$Br^{79}Br^{81}$	$2.283_6{}^a$	0.006_0	$0.129_4{}^c$	0.001_3	0.006_7	...	0.000_5	2.290_9	2.420_2
$I_2{}^{127}$	$2.666_6{}^a$	0.007_8	$0.449_7{}^c$	0.001_8	0.009_1	...	0.000_8	2.676_2	3.126_2

a The parameters necessary for the calculation of the terms in this row were obtained from G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1950) 2nd ed. Note that all calculations are based on pure isomeric forms of the diatomic molecules and that $l_\alpha{}^2=16.860z/\omega_e\mu_A$ and $a=1.355_7\times10^{-3}\omega_e(\mu_A/D_0{}^0)^{\frac{1}{2}}$ in Herzberg's units and notation.

b The r_e value in this case was obtained from the reference: W. G. Richards and R. F. Barrow, Proc. Chem. Soc. **1962**, 297.

c The large corrections in these cases are due to the term proportional to $a^3l_\alpha{}^4$ and may be due partly to the neglect of terms of the order C^4, C^2D, and D^2. To include these terms in the calculation would require the use of the third-order wavefunction.

reduces to

$$M(s) = Kc(s) \sum_{n=0}^{\infty} \exp[-(h\nu/2kT)(2n+1)]$$

$$\times \sum_{J=0}^{\infty} (2J+1) \exp[-(\hbar^2/2IkT)J(J+1)]$$

$$\times \int_0^{\infty} dr \mid Q_n{}^{(1)}(r,J) \mid^2 \sin(sr)/(sr). \quad (1.27)$$

The calculation of (1.27) may be simplified by using the expression for $\mid Q_n{}^{(1)}(r,J) \mid^2$

$$\mid Q_n{}^{(1)}(r,J) \mid^2 = Q_n{}^{(0)}(z)^2$$
$$+ C[z^3 + z(4n+1)][Q_n{}^{(0)}(z)^2/3B]$$
$$- C[z^2 + 2(2n+1)](2n+2)^{\frac{1}{2}}[Q_n{}^{(0)}(z)Q_{n+1}{}^{(0)}(z)/3B],$$
$$(1.28)$$

and expanding $1/r$ so that

$$1/r \cong (1/r_0)[1 - B^{-\frac{1}{2}}(z/r_0)]. \quad (1.29)$$

The sum over n in both the numerator and denominator can be evaluated before integrating over z. The sums can be easily evaluated by making use of the relation[13]

$$\sum_{n=0}^{\infty} \exp[-(h\nu/kT)(n+\frac{1}{2})]H_n{}^2(z) \exp(-z^2)/2^n n!$$

$$= \exp[-z^2 \tanh(h\nu/2kT)]/2 \cosh(h\nu/kT), \quad (1.30)$$

and the differentiation of (1.30) with respect to the parameter $(h\nu/kT)$. Further details are presented in Appendix II.

[13] See reference 12, Vol. I, p. 786.

The approximate result for $M(s)$ is

$$M(s) = c(s) \exp[-\frac{1}{2}s^2l_0{}^2 \coth(h\nu/2kT)]$$

$$\times [\sin(sr_0)A(T)/(sr_0) + \cos(sr_0)B(T)/(sr_0)], \quad (1.31)$$

where

$$r_0 \cong r_e + 4l_\alpha{}^4 \cot[\hbar/(2IkT)^{\frac{1}{2}}]/[r_e{}^3\hbar/(2IkT)^{\frac{1}{2}}], \quad (1.32)$$

$$l_0{}^2 \cong l_\alpha{}^2 + 6l_\alpha{}^6(a - 1/r_e)$$
$$\times \cot[\hbar/(2IkT)^{\frac{1}{2}}]/[r_e{}^3\hbar/(2IkT)^{\frac{1}{2}}] \quad (1.33)$$

$$A(T) = 1 - 3al_\alpha{}^2 \coth(h\nu/2kT)/(2r_0)$$
$$+ s^2al_\alpha{}^4[3 \coth^2(h\nu/2kT) - 1]/r_0, \quad (1.34)$$

and

$$B(T) = -sl_\alpha{}^2 \coth(h\nu/2kT)/r_0 + 3sal_\alpha{}^2 \frac{1}{2} \coth(h\nu/2kT)$$
$$- s^3al_\alpha{}^4 \frac{1}{6}[3 \coth^2(h\nu/2kT) - 2]. \quad (1.35)$$

Usually the factor $A(T)$ is taken to be nearly unity and the terms in $B(T)$ are incorporated into the phase of $\sin(s\, r_0)$. For cases where the above approximation is not adequate,[14] the $M(s)$ function should be characterized in terms of the more exact formulas derived in the next section of this paper.

MORSE MODEL FOR EXCITED VIBRATIONAL STATES

The approximate solutions to the Morse potential function,[15]

$$V(r) = D \exp[2a(r_e - r)] - 2D \exp[a(r_e - r)], \quad (2.0)$$

[14] Bartell has recently shown that the errors in (1.31) are of two types. The first is due to the truncation of the series expansion of the potential, and the second is due to errors in the perturbation approximation. Bartell's calculations for CH_4 and Cl_2 indicated that these errors were largely compensating at 300°K (L. S. Bartell, private communication).

[15] Reference 12, p. 1672.

TABLE II. Vibrational and vibration-rotation coupling contributions to l_e^2 at 300° and 1500°K for selected diatomic molecules.

	l_α[a]	$l_\alpha^2 \coth(h\nu/2kT)$		Vibrational contribution		Vibration-rotation coupling terms		l_e	
		$T=300°$K	$T=1500°$K	$T=300°$K	$T=1500°$K	$T=300°$K	$T=1500°$K	$T=300°$K	$T=1500°$K
H_2^1	0.087_2	0.007610_1	0.007838_4	0.000868_0	0.000949_0	0.000080_0	0.000458_2	0.092_5	0.096_2
H^1Cl^{35}	0.075_9	0.005755_1	0.006445_7	0.000451_0	0.000629_5	0.000049_5	0.000282_2	0.079_1	0.085_8
N_2^{14}	0.031_9	0.001020_2	0.001256_9	0.000028_6	0.000051_6	0.000003_8	0.000014_8	0.032_4	0.036_4
$N^{14}O^{16}$	0.034_4	0.001185_8	0.001640_0	0.000040_4	0.000096_9	0.000005_8	0.000041_5	0.035_1	0.042_2
O_2^{16}	0.036_5	0.001336_2	0.002241_7	0.000048_5	0.000183_0	0.000010_5	0.000097_1	0.037_4	0.050_2
Cl_2^{35}	0.041_3	0.001948_9	0.006450_7	0.000066_5	0.000970_0	0.000020_7	0.000812_4	0.045_1	0.090_7
$Br^{79}Br^{81}$	0.036_1	0.002007_9	0.008499_0	0.000077_3	0.001617_0	0.000024_8	0.003575_7	0.045_9	0.117_0[b]
I_2^{127}	0.035_2	0.002613_6	0.012072_5	0.000126_0	0.002915_0	0.000041_3	0.015674_0	0.052_7	0.175_1[b]

[a] See footnotes a and b of Table I.
[b] See footnote c of Table I.

have been given by Morse and can be written as

$$Q_n = N^{-1/2} z^{\alpha-n-\frac{1}{2}} \exp[-z/2] L_n^{2\alpha-2n-1}(z), \quad (2.1)$$

where z is $2\alpha \exp[a(r_e-r)]$, D is the dissociation energy, N and α are constants, and $L_n^{2\alpha-2n-1}(z)$ is an associated Laguerre polynomial. The effect of centrifugal distortion can be included approximately in this solution by approximating r_0^2/r^2 as[16]

$$r_0^2/r^2 \simeq (1-3/ar_0+3/a^2r_0^2) + (4/ar_0-6/a^2r_0^2)(z/2\alpha)$$

$$+ (-1/ar_0+3/a^2r_0^2)(z/2\alpha)^2, \quad (2.2)$$

where r_0 is the minimum of the combined potential used in the previous section. The complete potential $W(r)$ can then be approximated as

$$W(r) \cong J(J+1)(4/ar_0-6/a^2r_0^2) \exp[a(r_0-r)]/r_0^2$$

$$+ J(J+1)(1/ar_0-3/a^2r_0^2)$$

$$\times \exp[2a(r_0-r)]/r_0^2 + 2\mu V(r_0-r)/\hbar^2. \quad (2.3)$$

The definition of α in (2.1) now becomes

$$\alpha = 1/(2a^2l_\alpha^2) - 3l_\alpha^2 J(J+1)[1-1/ar_0]/(ar_0^3) \quad (2.4)$$

and the $M(s)$ function can be calculated quite readily by employing the following scheme. First, the normalization integral can be shown to be

$$N = \int_0^\infty dz \exp(-z) z^{(P_n-1)} [L_n^{P_n}(z)]^2$$

$$= \Gamma(1+P_n+n)/(n! \, P_n), \quad (2.5)$$

where P_n is $2\alpha-2n-1$. The general solution to inte-

grals of this type has been given as[17]

$$\int_0^\infty dz \exp(-z) z^{(P_n+B)} [L_n^{P_n}(z)]^2$$

$$= (-1)^n \Gamma(1+P_n+n) \sum_{r=0}^n (-1)^r \begin{bmatrix} B+r \\ n \end{bmatrix}$$

$$\times \Gamma(P_n+B+r+1)/[r!\Gamma(n-r+1)\Gamma(1+P_n+r)], \quad (2.6)$$

where B may be a complex number, and the long brackets indicate a bionomial coefficient.

The $M(s)$ function for the nth excited vibrational state can then be written as

$$M_n(s) = N^{-1} \int_0^\infty dz \exp(-z) z^{(P_n-1)} [L_n^{P_n}(z)]^2$$

$$\times j_0\{s[r_e-a^{-1}\ln(z/2\alpha)]\}, \quad (2.7)$$

where the function $j_0(x)$ is a spherical Bessel function of order zero. The integral over z can be easily evaluated if the function $j_0(x)$ is represented by its integral transform[18] and the integration over z carried out so that

$$M_n(s) = \frac{1}{2} P_n \int_{-1}^1 dt \exp(isr_e t)(2\alpha)^{ist/a} F_n(t), \quad (2.8)$$

where

$$F_n(t) = (-1)^n \sum_{r=0}^n (-1)^r \Gamma(P_n-ist/a+r)$$

$$\times \Gamma(r-ist/a)/[r!\Gamma(-ist/a-n+r)\Gamma(n-r+1)$$

$$\times \Gamma(1+P_n+r)]. \quad (2.9)$$

The $F_n(t)$ function for the ground and first two excited

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[16] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955), p. 8.

[17] H. Buchholz, *Die Konfluente Hypergeometrische Funktion* (Springer-Verlag, Berlin, 1953), p. 143, formulas 20 and 21.
[18] See reference 12, p. 1575.

vibrational states is

$$F_0(t) = \Gamma(P_0 - ist/a)/\Gamma(P_0+1), \quad (2.10)$$

$$F_1(t) = [\Gamma(P_1 - ist/a)/\Gamma(P_1+1)]$$
$$\times [1 + (ist/a - s^2t^2/a^2)/(P_1+1)], \quad (2.11)$$

and

$$F_2(t) = [\Gamma(P_2 - ist/a)/\Gamma(P_2+1)]$$
$$\times \{1 + 2(ist/a - s^2t^2/a^2)/(P_2+1)$$
$$- [(ist/a) - (s^2t^2/2a^2) + (is^3t^3/a^3)$$
$$- (s^4t^4/2a^4)]/[(P_2+2)(P_2+1)]\}. \quad (2.12)$$

Since P_n is a very large parameter in the above cases, it is possible to expand the gamma functions in powers of $(ist/P_n a)$ and perform the integrations over t. The details of this expansion are given in Appendix II. The application of this procedure to the expressions for $M_n(s)$ given above result in the approximate formulas

$$M_0(U_0) \cong \exp[-A_2+A_4]$$
$$\times \sin[U_0 - 2A_2/U_0 - A_3 + A_5]/[U_0 - 2A_2/U_0 + 2A_2^2/U_0],$$
$$(2.13)$$

$$M_1(U_1) \cong M_0(U_1) + sal_\alpha^2(d/dU_1)M_0(U_1)$$
$$+ s^2l_\alpha^2(d/dU_1)^2M_0(U_1), \quad (2.14)$$

and

$$M_2(U_2) \cong M_0(U_2) + 2sal_\alpha^2(d/dU_2)M_0(U_2)$$
$$+ 2s^2l_\alpha^2(d/dU_2)^2M_0(U_2) - sa^3l_\alpha^4(d/dU_2)M_0(U_2)$$
$$- s^2a^2l_\alpha^4(d/dU_2)^2M_0(U_2) + s^3al_\alpha^4(d/dU_2)^3M_0(U_2)$$
$$+ \tfrac{1}{2}(s^4l_\alpha^4)(d/dU_2)^4M_0(U_2), \quad (2.15)$$

where

$$U_n \cong s\{r_e + 4l_\alpha^4 J(J+1)/r_e^3 + al_\alpha^2 \tfrac{1}{2}(4n+3)$$
$$+ 3a^2l_\alpha^6 J(J+1)(4n+3)[(1-1/ar_e)/r_e^3]$$
$$+ a^3l_\alpha^4 \tfrac{1}{12}(24n^2+36n+13) + \cdots\}, \quad (2.16)$$

$$A_2 \cong s^2\{l_\alpha^2/2 + 3al_\alpha^6 J(J+1)[(1-1/ar_e)/r_e^3]$$
$$+ a^2l_\alpha^4 \tfrac{1}{4}(4n+3)$$
$$+ 3a^3l_\alpha^8 J(J+1)(4n+3)[(1-1/ar_e)/r_e^3] + \cdots\},$$
$$(2.17)$$

$$A_3 \cong s^3\{(al_\alpha^4/6) + (2a^2l_\alpha^8)[J(J+1)(1-1/ar_e)/r_e^3]$$
$$+ a^3l_\alpha^6 \tfrac{1}{6}(4n+3) + \cdots\}, \quad (2.18)$$

$$A_4 \cong s^4(a^2l_\alpha^6/12 + \cdots), \quad (2.19)$$

and

$$A_5 \cong s^5(a^3l_\alpha^8/20 + \cdots). \quad (2.20)$$

It is also possible to simplify (2.13) by defining an effective bond length, r_m, and an effective amplitude of vibration, l_m, such that

$$r_m = (U_n - 2A_2/U_n)/s \quad (2.21)$$

and

$$l_m^2 = 2(A_2 - A_4)/s^2. \quad (2.22)$$

Using this notation, (2.13) reduces to

$$M_0(s) \cong \exp(-l_m^2s^2/2)$$
$$\times \sin[(sr_m - A_3 + A_5)/(sr_m + 2A_2^2/U_0)]. \quad (2.23)$$

It is easily seen that the main terms in (2.21), (2.22) and (2.23) check with those given by Kuchitsu and Bartell.[2] As a check of the approach used here, both r_g and l_e^2 were computed for the ground vibrational state where $J=0$. To do this, the term $\ln(z/2\alpha)^{-1/a}$ was expanded in the usual series for a logarithm[19]

$$\ln(z/2\alpha)^{-1/a} = [(z/2\alpha)^{-1/a} - 1]$$
$$- \tfrac{1}{2}[(z/2\alpha)^{-1/a} - 1]^2 + \cdots, \quad (2.24)$$

keeping only the first two terms. Using this approximation, r_g and l_e^2 were found to be

$$r_g = r_e + \tfrac{3}{2}al_\alpha^2 + \tfrac{13}{12}a^3l_\alpha^4 + \tfrac{11}{12}a^5l_\alpha^6 - \tfrac{11}{6}(al_\alpha^4/r_e^2) \quad (2.25)$$

and

$$l_e^2 = l_\alpha^2 + \tfrac{15}{4}a^2l_\alpha^4 + \tfrac{59}{12}a^4l_\alpha^6 - (2l_\alpha^4/r_e^2). \quad (2.26)$$

The expression for r_g agrees with that given in reference 2 to the first three terms and with the first two terms in l_e^2. It should be noted that the approximation used here in the expansion of the $\log(z/2\alpha)^{-1/a}$ term does not enter into the calculation of the $M_n(s)$ function.

CONCLUSIONS

A detailed study of the effects of temperature on the reduced molecular intensity function has been presented. For diffraction work at room temperature, it has been shown that the effects of centrifugal distortion are much smaller than those due to anharmonic vibrations. In the case of the electron diffraction parameter, r_g, the effect of centrifugal distortion can be characterized accurately by the usual classical treatment over a wide range of temperatures for most molecules. The main exceptions are hydrogen and the lighter hydrides where a more exact treatment is needed at lower temperatures (see Appendix I).

The parameter l_e at room temperature is not effected by centrifugal distortion, but corrections of the order of 0.0002 Å may result from a coupling of the vibrational and rotational effects. At higher temperatures, this coupling between vibrational and rotational effects can become quite large and would have to be considered in precise work.

In the case of the halogens, rotational and vibrational effects produce appreciable corrections to diffraction data even at room temperature. For higher temperatures, the corrections to diffraction parameters become extremely large and the calculations presented

19 C. D. Hodgman, *Mathematical Tables* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1948), 9th Ed., p. 279.

here indicate that at 1500°K, a third-order perturbation treatment may be necessary.

Expressions for the $M(s)$ function have also been obtained and it should be possible with the use of these to characterize experimental scattering curves for diatomic molecules over a wide temperature range.

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APPENDIX I

The sum over rotational states,

$$S(J) = \sum_{J=0}^{\infty} (2J+1) \exp[-(\hbar^2/2IkT)J(J+1)], \quad (3.0)$$

has been approximately evaluated[20] and can be written as

$$\sum_{J=0}^{\infty} (2J+1) \exp[-(\hbar^2/2IkT)J(J+1)]$$
$$= (2IkT/\hbar^2) + \tfrac{1}{3} + \tfrac{1}{15}(\hbar^2/2IkT)$$
$$+ \tfrac{4}{315}(\hbar^2/2IkT)^2 + \cdots. \quad (3.1)$$

The series expansion for the $\csc^2 x$ can be written as[21]

$$\csc^2 x = (1/x^2) + \tfrac{1}{3} + (x^2/15) + 10(x^4/945), \quad (3.2)$$

so that to very good approximation, the sum in (3.1) can be written as

$$\sum_{J=0}^{\infty} (2J+1) \exp[-(\hbar^2/2IkT)J(J+1)]$$
$$= \csc^2[\hbar/(2IkT)^{\frac{1}{2}}]. \quad (3.3)$$

APPENDIX II

Integrals of the type

$$A(\alpha) = \int_{-\infty}^{\infty} dz \exp(-z^2) H_n(z) H_{n+1}(z) \sin(\alpha z), \quad (4.0)$$

$$B(\alpha) = \int_{-\infty}^{\infty} dz \exp(-z^2) H_n(z) H_{n-1}(z) \sin(\alpha z), \quad (4.1)$$

can be evaluated by using the following well-known relations among Hermite polynomials[13]

$$zH_n(z) = nH_{n-1}(z) + \tfrac{1}{2}[H_{n+1}(z)], \quad (4.2)$$

$$(d/dz)H_n(z) = 2nH_{n-1}(z), \quad (4.3)$$

and

$$(d/dz)[\exp(-z^2)H_n(z)] = -\exp(-z^2)H_{n+1}(z). \quad (4.4)$$

Eliminating $H_{n+1}(z)$ in (4.0) by using (4.2), it can easily be shown that

$$A(\alpha) = -2nB(\alpha) - 2(d/d\alpha)I(\alpha), \quad (4.5)$$

where

$$I(\alpha) = \int_{-\infty}^{\infty} dz \exp(-z^2)[H_n(z)]^2 \cos\alpha z. \quad (4.6)$$

A second equation can be obtained by using relations (4.4) and (4.3) with $A(\alpha)$ and then integrating by parts. This results in the second relation,

$$A(\alpha) = \alpha I(\alpha) + 2nB(\alpha), \quad (4.7)$$

so that $A(\alpha)$ may be obtained solely in terms of $I(\alpha)$ as

$$A(\alpha) = \tfrac{1}{2}\alpha I(\alpha) - (d/d\alpha)I(\alpha). \quad (4.8)$$

By use of (4.2) all the integrals encountered in this work may be reduced to either $A(\alpha)$ or $I(\alpha)$.

APPENDIX III

The term $\Gamma(P_n - ist/a)/\Gamma(P_n+1)$ which occurs in equations (2.10) through (2.12) can be very accurately approximated by use of the gamma function expansion.[22]

$$\Gamma(z) = (2\pi)^{\frac{1}{2}} z^{-\frac{1}{2}} \exp(-z+z \ln z)\left(1 + \frac{1}{12z} + \frac{1}{288z^2} - \cdots\right). \quad (5.0)$$

This results in the approximate relation

$$\Gamma(z+\epsilon)/\Gamma(z) \cong z^\epsilon \exp\{-(\epsilon/2z)[1+(6z)^{-1}]$$
$$+ (\epsilon^2/2z)[1+(2z)^{-1}+(6z^2)^{-1}]$$
$$- (\epsilon^3/6z^2)(1+z^{-1}) + (\epsilon^4/12z^3)[1+(3/2z)]$$
$$- (\epsilon^5/20z^4)[1+(2/z)]\}, \quad (5.1)$$

where $z \gg \epsilon$ and which is accurate through terms of order $1/z^2$ in Eq. (5.0).

It should be pointed out also that all the necessary integrals needed in the calculation of the $M_n(s)$ functions can be obtained approximately from the integral

$$\frac{1}{2}\int_{-1}^{1} dt \exp(iU_n t - A_2 t^2)$$
$$\cong \exp(-A_2)[\sin(U_n)/U_n][1 + (2A_2/U_n^2)(1-2A_2)$$
$$+ (4A_2^2/U_n^4)(4A_2^2 - 12A_2 + 3) \cdots]$$
$$- \exp(-A_2)[\cos(U_n)/U_n]\{(2A_2/U_n)$$
$$\times [1 + (2A_2/U_n^2)(3-2A_2)$$
$$+ (4A_2^2/U_n^4)(4A_2^2 - 20A_2 + 15) \cdots]\}. \quad (5.2)$$

[20] See for instance, S. Golden, *Introduction to Theoretical Chemistry* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1961), p. 134.

[21] B. O. Pierce, *A Short Table of Integrals* (Ginn and Company, Boston, Massachusetts, 1929), The expansion for the $\csc^2 x$ may be obtained from Eq. 775, p. 91 by taking the negative first derivative term by term.

[22] E. Jahnke and R. Emde, *Funktionentafeln* (Dover Publications, Inc., New York, 1945), 4th Ed., p. 10.