168
3-10-75

DL-1184

UCRL-51674

**ESTIMATED INFRARED SPECTRA
OF CRYOGENIC D_2 -DT- T_2**

P. C. Souers
R. G. Hickman
W. Z. Wade
R. T. Tsugawa

January 3, 1975

MASTER

Prepared for U.S. Atomic Energy Commission under contract No. W-7405-Eng-48

**LAWRENCE
LIVERMORE
LABORATORY**

University of California/Livermore

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$ ____*; Microfiche \$1.45

<u>* Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

LAWRENCE LIVERMORE LABORATORY
University of California, Livermore, California, 94550

UCRL-51674

**ESTIMATED INFRARED SPECTRA
OF CRYOGENIC D₂-DT-T₂**

P. C. Souers
R. G. Hickman
W. Z. Wade
R. T. Tsugawa

MS, date: January 3, 1975

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

204

Contents

Abstract	1
Introduction	1
Basic Vibration-Rotation Properties of Hydrogen	2
Simple Vibration-Rotation Calculations for Hydrogen	4
Other Measured Infrared Spectra	6
Estimated Spectrum for D ₂ -DT-T ₂ Liquid	10
Conclusion	11
Acknowledgments	11
References	12

ESTIMATED INFRARED SPECTRA OF CRYOGENIC D₂-DT-T₂

Abstract

The literature on the fundamental infrared vibration-rotation spectra of cryogenic H₂, HD, and D₂ is reviewed. The assignments of the most basic spectral lines are given relative to the vibrational and rotational energy levels. Emphasis is given to changes of spectral appearance upon liquefaction and freezing. Using simple models, the vibrational and rotational splittings of DT and T₂ are calculated. All data is used to estimate the spectrum of D₂-DT-T₂ liquid at the triple-line temperature of 19.75K. It is

seen that quantitative analysis of the three components may be carried out, as well as measurement of the ortho-para transition rates. The chemical equilibrium rates are probably not measurable, however, unless liquid D₂ and T₂ are actually mixed. Similar information should be available from the spectrum of the solid; however, the chemical-equilibrium constant has not been calculated at low temperatures. Induced infrared appears most promising as a tool for phase-diagram studies of the cryogenic system D₂-DT-T₂.

Introduction

The current interest in laser-induced hydrogen fusion¹⁻³ has revived interest in the basic properties of the heavy hydrogen fuel. The sculpturing of the laser microtargets to desired geometries can probably only be accomplished by liquefying or freezing the hydrogen. Hence, cryogenic properties become of great interest. We have recently completed a model of the D₂-DT-T₂ phase diagram and compiled many of the physical properties of heavy hydrogen.⁴ As might be expected, few properties have been measured on DT and T₂ because of the radioactivity.

Some special problems may arise because D-T is in reality a mixture of the three components, D₂, DT, and T₂,

catalyzed to chemical equilibrium by the tritium beta particle.⁴ It becomes of interest, therefore, to seek physical methods that differentiate between the three chemical species plus, as described below, their metastable rotational states. Induced fundamental infrared spectroscopy seems a promising tool in this regard.⁵ We shall here review the literature, and derive by simple means the spectra expected for the mixture D₂-DT-T₂.

* Others closely related are infrared harmonic vibrational-rotational and pure rotational spectra, and also the Raman sidebands of vibrational-rotational lines.

Basic Vibration-Rotation Properties of Hydrogen

Hydrogen, regardless of isotopic species, forms a diatomic molecule, which vibrates with a single mode. Our infrared review covers the range of 2-5 μm , which is the fundamental vibrational mode; i.e., the molecule is excited from the ground state (vibrational quantum number, $v = 0$) to the first excited state ($v = 1$).

It is surprising that molecules with identical atoms (H_2 , D_2 , or T_2) can possess an infrared spectrum at all, since these molecules possess no permanent dipole moment and should not interact with the electric field of incident infrared radiation. This probably is true for a single isolated molecule, but the presence of neighbor molecules, with their perturbing electric fields, causes the creation of a transient electric-dipole moment in H_2 .⁵ This induced moment can interact with radiation, albeit weakly, and a measurable infrared spectrum results.

As might be expected, the denser the form of hydrogen, the more the neighboring molecules interact with each other, and the stronger is the induced infrared spectrum. In the gas phase, the spectral amplitude increases as the square of the density.⁵ At 0.10 MPa (1 atm), an experimental path length of up to 13.6 m was used to obtain sufficient absorption.⁵ Upon conversion to liquid or solid, only a few millimeters of thickness is required.⁶

The rotational mode of the hydrogen molecule interacts with the vibrational. The $v = 0 \rightarrow 1$ vibrational line thus exhibits fine structure due to rotational

transitions taking place at the same time. This structure will be explored in detail in the next section. Its importance is that it identifies the ground rotational state from the metastable first excited state.

One peculiarity is found for H_2 , D_2 and T_2 . The fast rotational transitions are only those for which $\Delta J = 0, \pm 2, \pm 4, \dots$. The transitions $\Delta J = \pm 1, \pm 3, \dots$ are essentially forbidden and proceed very slowly — over periods of days and weeks.⁷ For HD, HT, and DT, the $\Delta J = \pm 1, \pm 3, \dots$ transition is allowed by the small permanent difference between the atoms. The rotational transitions, therefore, take place rapidly.

The importance of these transitions lies in two facts. First, the energy locked up in the rotational mode is very large for hydrogen because the mass is so small (e.g., H_2 has the largest rotational energy with room-temperature rotational energy about equal to the heat of vaporization).⁸ Upon cooling of HD, HT, and DT, this energy, although fairly large, comes out quickly, because the rotational levels can de-excite by $\Delta J = -1$ transitions. But H_2 , D_2 , and T_2 cannot de-excite quickly, because the $\Delta J = -1$ transition is so slow. Molecules with $J = 1$ are trapped in a metastable state, although thermodynamically we expect them to fall to the $J = 0$ ground state.

Because of the large rotational energies and the metastable states of H_2 , D_2 , and T_2 , it has become common to speak of two "kinds" of each of these molecular species: ortho (o) and para (p). Table 1 summarizes the definitions of these terms.

The ortho and para variations occur because the rotational moments of H_2 , D_2 , and T_2 are locked to the nuclear magnetic moments. For H_2 and T_2 , the even rotational states are locked to the molecular nuclear spin, I , of zero (anti-parallel alignment of two spin-1/2 nuclei); the odd rotational states are locked to the nuclear spin state of 1 (parallel alignment). At low temperatures, all molecules eventually lose their rotational energy and fall to the $J = 0$ ground state ($I = 0$). Thus, we have 100% pH_2 and pT_2 at 0 K. At very high temperatures, both odd and even rotational states will be filled. The distribution will be set by the number of nuclear magnetic states, equal to $2I + 1$. So pH_2 and pT_2 ($I = 0$) have one state each; oH_2 and oT_2 ($I = 0$) have three. We expect and find 25% para and 75% ortho at high temperatures. We note that the para form with no nuclear moment ($I = 0$) cannot be seen by nuclear magnetic

resonance (NMR); the ortho form ($I = 1$) can.

D_2 is somewhat different, because each nucleus has a spin of 1. The two nuclear spins combine to yield states of $I = 0, 1$, and 2, which are found to be locked to the even, odd, and even rotational levels, respectively. At 0 K, all molecules fall again to the $J = 0$ state, which is called "ortho" for D_2 — the opposite from H_2 and T_2 . At high temperatures, the nuclear states are all equally filled. There are eight, since $I = 0, 1$, and 2 yields 1, 3, and 5 nuclear magnetic states. Since states $I = 0$ and 2 are associated with ortho, we expect 66-2/3% oD_2 and 33-1/3% pD_2 at high temperatures. Only the $I = 0$ form of oD_2 is inactive to NMR.

It is of interest to inquire why the definitions of ortho and para are reversed for H_2/T_2 and D_2 . The reason stems from the first studies of hydrogen at

Table 1. Definition of ortho and para hydrogen.

	Rotational quantum numbers, J	Fraction at 0 K (%)	Molecular nuclear spin, I	Number of magnetic states, $2I + 1$	Fraction at high temp (%)	NMR ^a active?
H_2 and T_2			$(1/2 + 1/2)$			
Para (p)	$J = 0, 2, 4, \dots$ even/symmetric	100	0	1	25	No
Ortho (o)	$J = 1, 3, 5, \dots$ odd/antisymmetric	0	1	3	75	Yes
D_2			$(1 + 1)$			
Ortho (o)	$J = 0, 2, 4, \dots$ even/symmetric	100	0, 2	1, 5	66-2/3	No, yes
Para (p)	$J = 1, 3, 5, \dots$ odd/antisymmetric	0	1	3	33-1/3	Yes
H_2 , D_2 , and T_2						
Normal (n)	The equilibrium mixture of o-p forms at room temperature (close to "high-temperature" percentage).					
Equilibrium (e)	The equilibrium mixture of o-p forms at any temperature except room temperature.					

^aNuclear magnetic resonance.

room temperature, where the percentage of states is essentially that of "high temperature" (Table 1). The ortho form was defined as the form found in greater quantity at room temperature, and the para as the form found in lesser quantity. A glance at the "high-temperature" column of Table 1 will show how the assignments were made. Only later was the correlation with the rotational states

discovered. The ortho-para terminology, although somewhat confusing, continues to be used for H₂, HT, and DT.

Two other points of terminology should be clarified. The equilibrium o-p mixture at room temperature is called "normal" (n) hydrogen. The equilibrium o-p mixture at any other temperature than room temperature is called "equilibrium" (e) hydrogen.

Simple Vibration-Rotation Properties of Hydrogen

Figure 1 shows the experimental fundamental infrared spectrum for gaseous nH₂.⁵ The x-axis is frequency (Hz); the y-axis is the absorption coefficient, α (m⁻¹), defined by the property of exponential absorption of energy. We have

$$I = I_0 \exp(-\alpha x), \quad (1)$$

where I_0 is the input intensity, I the output intensity, x the thickness of the sample, and α the absorption coefficient. Then

$$\alpha = \frac{1}{x} \ln \frac{I_0}{I}. \quad (2)$$

Figure 1 is important because it shows the basic three-peak rotational structure, which sharpens considerably at cryogenic temperatures. These peaks are called Q, S(0), and S(1),⁶ reading from left to right. Figure 2 shows whence these major lines arise. The Q peak is $\Delta J = 0$ and is found to stem mostly from the $J = 1 \rightarrow 1$ transition but partly from $J = 0 \rightarrow 0$. The S peaks come from $\Delta J = +2$ transitions.

A subscript 1 may be added to the notation, indicating the fundamental vibrational transition, $v = 0 \rightarrow 1$. We shall omit this notation except for figures showing double transitions.

Fig. 1. Basic three-peak fundamental vibration-rotation spectra as shown by gaseous nH₂ at 1.4 MPa (200 atm).⁵

S(0) comes from $J = 0 \rightarrow 2$, and S(1) from $J = 1 \rightarrow 3$. Only these levels are important at cryogenic temperatures; at high temperatures and pressures, $J = \pm 4$ transitions, called S(2) and S(3), result,

Fig. 2. Energy-level diagram for fundamental vibration-rotation excitations in hydrogen.

In calculating the basic spectrum of Fig. 1, we may consider the hydrogen molecule to be a harmonic oscillator, vibrating at a frequency, ν :

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \quad (3)$$

where k is the force constant (N/m), and μ is the reduced mass of the molecule

(kg).^{9,10} Using the $\Delta J = 0$ experimental (gaseous) infrared frequencies after Herzberg,¹¹ we may calculate the corresponding force constants. Then we estimate both the force constant and basic vibrational frequency for DT, the only missing species in the Herzberg list. This data is listed in Table 2, which shows that the frequency decreases (red shift) with increasing mass.

The amplitude of the vibrational band may be estimated for the various hydrogen species from the classical maximum amplitude of the first excited vibrational states, S_1 . This is:

$$S_1 = \frac{3h\nu}{2k}, \quad (4)$$

where h is Planck's constant.¹² This is calculated in Table 2, where the column relative to H_2 as 1 is most pertinent. It shows that, for a given density of molecules, one may expect the infrared spectral amplitude to decrease with increasing mass. The T_2 spectrum has about three-fourths the amplitude of the H_2 spectrum.

Next, we wish to obtain a simple measure of the rotational splitting leading to the three peaks of Fig. 1. The frequency shift caused by the rotational

Table 2. Basic vibrational-rotational data according to Herzberg.¹¹

	Reduced mass, μ (10^{-27} kg)	Vibrational frequency, ν (10^{14} Hz)	Wavelength, λ (μ m)	Force constant, k (10^2 N/m)	Classical maximum vibrational amplitude, S_1		Rotational constant, B_e (10^{12} Hz)	Frequency shift (10^{12} Hz)	
					(10^{-11} m)	Relative		$J = 0 \rightarrow 2$	$J = 1 \rightarrow 3$
H_2	0.8369	1.318	2.275	5.734	1.511	1.00	1.023	9.11	18.23
HD	1.116	1.144	2.620	5.765	1.405	0.93	1.369	6.84	13.69
HT	1.255	1.082	2.771	5.793	1.362	0.90	1.216	6.08	12.16
D_2	1.673	0.935	3.207	5.768	1.269	0.84	0.912	4.56	9.12
DT	2.020	0.851 ^a	3.52 ^a	5.76 ^a	1.210 ^a	0.80 ^a	0.764 ^a	3.82 ^a	7.64 ^a
T_2	2.505	0.766	3.916	5.793	1.146	0.76	0.609	3.05	6.09

^aEstimated.

transition $J \rightarrow J'$ is approximately

$$\Delta\nu(J \rightarrow J') = B_e [J'(J' + 1) - J(J + 1)] \quad (5)$$

where B_e is Herzberg's rotational constant.^{11,13} This frequency shift may be calculated for the transitions $J = 0 \rightarrow 2$ and $1 \rightarrow 3$. The results are listed in Table 2.

Herzberg's listed $\Delta J = 0$ frequencies do not quite correspond to the actual Q^{-1} branch frequencies, ν_Q , found in the dense gas of Fig. 1. We take the actual values for H_2 , HD, and D_2 , summarized in Table 3, as the zero-point reference, and linearly readjust the expected ν_Q 's of the unmeasured species DT and T_2 by the relationship calculated from the Herz-

berg data. We also compute the frequency shifts, $(\nu_{S(1)} - \nu_Q)$ and $(\nu_{S(0)} - \nu_Q)$, for the experimental H_2 , HD, and D_2 data. The experimental shifts of Table 3^{5,6,14-17} are in good agreement with the calculated ones of Table 2. This allows us to extrapolate the data to compute the $\nu_{S(0)}$ and $\nu_{S(1)}$ frequencies for DT and T_2 .

The expected frequencies of the basic three-peak infrared spectrum are listed for various species in Table 3. We see that for the mixture D_2 -DT- T_2 none of the frequencies overlap, but the outer wings of the outer peaks should cover each other to some extent. Despite this, it appears that the composite D_2 -DT- T_2 spectrum can indeed be resolved into its components.

Table 3. Experimental fundamental vibrational-rotational frequencies for dense hydrogen gas.^{5,6,14-17}

	Frequency, ν (10^{14} Hz), and wavelength, λ (μm)						Frequency shift (10^{12} Hz)	
	Q		S(0)		S(1)		J = 0 $\rightarrow$ 2	J = 1 $\rightarrow$ 3
	ν	λ	ν	λ	ν	λ		
H_2	1.26	2.38	1.36	2.20	1.43	2.10	10	17
HD	1.09	2.75	1.17	2.56	1.22	2.46	8.0	13
D_2	0.904	3.32	0.952	3.15	0.987	3.04	4.8	8.3
DT ^a	0.816	3.68	0.854	3.51	0.892	3.36	3.8	7.6
T_2 ^a	0.734	4.09	0.764	3.93	0.795	3.77	3.0	6.1

^a Estimated.

Other Measured Infrared Spectra

We shall now observe other spectra to explore the range of information given by infrared spectroscopy. All of the work listed in this report has been done in a remarkable 10-year effort under H. L. Welsh at the University of Toronto.

Figure 3 shows the familiar three-peak spectrum for H_2 gas at 20.4 K as the para concentration increases from 50% to 98%.¹⁵ The Q(1) and S(1) peaks due to oH_2 virtually vanish, leaving a small Q(0) and a large central S(0) peak. It is

Fig. 3. Change in three-peak amplitudes due to a 48% increase in pD_2 , for gas at 20.4 K and 1.4 MPa (200 atm).¹⁵

easy to see that, with proper calibration, o-p concentrations and reaction rates could be measured, and such an analysis has been recently reported.¹⁶

Figure 4 shows the full gamut of spectra for gaseous, liquid, and solid nH_2 , taken with low resolution.⁶ The 78-K gas spectrum is the familiar three-peak type. However, even its Q-peak shows a shoulder. The feature Q_Q represents the pure $\Delta J = 0$ transition. Q_P and Q_R represent sidebands modulated by collisions in the dense gas and liquid and by phonons in the solid.⁶ The change of the Q-line from one peak in the 20.4-K gas of Fig. 3 to the well-defined Q_Q - Q_R split of the 17.5-K liquid in Fig. 4 suggests that the gas-liquid phase boundary may be experimentally located by infrared

spectroscopy. Recent high-resolution work has shown fine structure on the gas peaks,¹⁸ but it is certainly not as obvious as the wide splittings of Fig. 4.

From Fig. 4, we see that the two S peaks each split into two new peaks upon solidification. This suggests a means of locating the liquid-solid phase boundary. The main peaks are the S(0) and S(1) originals, with pure $\Delta J = 2$ rotational transitions. The new peaks $S_L(0)$ and $S_R(1)$ are transitions including lattice phonons.⁶

A new feature also appears in Fig. 4: the double transitions $2S(0)$, $S(0) + S(1)$, and $2S(1)$. These are assigned to transitions in which one molecule executes a vibration-rotational transition ($v = 0 \rightarrow 1$) as a second molecule simultaneously undergoes a pure rotational transition while in the ground vibrational state ($v = 0$).

Figure 5 shows a 77-K gas spectrum for HD.¹⁷ The basic three-peak structure is there and represents the transitions already described. The outer peaks are low because they mainly represent the $J = 1$ state, which is not greatly populated at 77 K. Further cooling puts virtually all molecules into the $J = 0$ level, and the central S(0) peak predominates.¹⁴ This is important because we may expect cryogenic DT to show mostly a strong central Si(0) peak, thereby reducing the problem of spectral overlap with D_2 and T_2 . The very small P(1), R(0), and R(1) lines are assigned to the $\Delta J = \pm 1$ transitions.¹³ It is interesting that the $\Delta J = \pm 1$ transitions, allowed for the HD molecule, do not appear more pronounced in the infrared spectrum.

Figure 6 shows the spectrum of solid D_2 with good resolution.¹⁴ There is not

Fig. 4. Fundamental vibration-rotation spectra for gaseous, liquid, and solid $n\text{H}_2$.⁶ Note that the y-axis is simply $\log(I_0/I)$; without knowing the thickness of the sample, one cannot derive the absorption coefficient.

much difference between the $n\text{D}_2$ and 97%-ortho spectra, since a $p \rightarrow o$ transition of only 30% of the molecules is involved. Upon transformation, however, the outer peaks diminish. We have seen how transitions to the $J = 0$ level at cryogenic temperatures strengthen the central $S(0)$ peak for H_2 , HD , and D_2 ;

this effect should occur for D_2 - DT - T_2 and diminish the spectral overlap.

The extreme detail shown by the high resolution of Fig. 6 suggests that lower resolution might be helpful in phase-diagram or concentration studies by obscuring the myriad of fine-structure lines.

Fig. 5. Fundamental vibration-rotation spectrum for HD gas at 77 K and 6.2 MPa (61 atm).¹⁷

Fig. 6. High-resolution infrared spectrum of solid D_2 .¹⁴

Estimated Spectrum for D₂-DT-T₂ Liquid

We may now summarize our knowledge to estimate the fundamental infrared spectrum of 1:1-D:T liquid D₂-DT-T₂ on the triple line at 19.75 K.⁴ Two spectra are shown in Fig. 7; both assume immediate de-excitation of the DT to about 10% J = 1 state at cryogenic temperatures. One spectrum assumes that the room-temperature properties have been frozen in; i.e., we have nD₂-DT-nT₂ in the amounts 25.3, 49.4, and 25.3% (chemical equilibrium constant, $K = 3.82$).⁴ The other spectrum assumes equilibration at 19.75 K, with eD₂-DT-eT₂ in the amounts

of 29.9, 40.2, and 29.9% ($K = 1.8$).⁴ The equilibrium form will probably occur fairly quickly upon liquefaction. The ortho-para transition in solid T₂ is known to proceed with a half-life of 17-100 minutes.^{19,20} No work has been published on the chemical equilibrium rate, but workers in the tritium-handling field feel that it, too, may be a matter of minutes.⁴

Figure 7 shows that the three species of heavy hydrogen will be recognizable and probably susceptible to quantitative measurements of relative amounts. This might allow the amount of tritium

Fig. 7. Estimated low-resolution infrared spectra of liquid D₂-DT-T₂ at 19.75 K.

enrichment upon liquefaction to be measured. It may also be possible to measure ortho-para rates for H_2 and T_2 , since the peak changes are relatively large. However, the chemical-equilibrium constant* does not change enough upon liquefaction to allow measurement of the reaction rates. To obtain this data, it may be necessary to actually mix liquid D_2 and T_2 .

* Actually calculated for 0.1 MPa (1 atm) gas; see Ref. 21.

The spectra of solid D_2 -DT- T_2 should look quite similar to Fig. 7, except that the outer peaks of the T_2 band would be lower because more molecules are in the $J = 0$ state. Unknown, however, is the chemical-equilibrium constant, which could drop precipitously at low temperatures, thereby depleting the DT bands. It seems risky to extrapolate existing chemical-equilibrium constants much below the triple line at 19.75 K. Hence, we shall not hazard a guess as to the appearance of the solid spectrum.

Conclusion

It appears that fundamental induced-infrared spectra will indeed be a useful tool in the quantitative study of cryogenic D_2 -DT- T_2 , especially in the vicinity of the triple line. A liquid or solid sample up to 1 cm thick will probably be required.

Acknowledgments

We should like to thank C. Hendricks and J. Emmett for their continuing interest in and support of these studies of the basic cryogenic properties of hydrogen isotopes.

References

1. J. Nuckolls, L. Wood, A. Thiessen, and G. Zimmerman, Nature **239**, 139 (1972).
2. J. Nuckolls, J. Emmett, and L. Wood, "Laser Induced Thermonuclear Fusion," Physics Today **26**, No. 8, 46 (August 1973).
3. J. Emmett, J. Nuckolls, and L. Wood, "Fusion Power by Laser Implosion," Scientific American **230**, No. 6, 24 (June 1974).
4. P. C. Souers, R. G. Hickman, W. Z. Wade, and R. T. Tsugawa, A Simple Model of D_2 -DT- T_2 Equilibrium at Cryogenic Temperatures, Lawrence Livermore Laboratory, Rept. UCRL-51681 (1974).
5. A. Watanabe and H. L. Welsh, Can. J. Phys. **43**, 818 (1965).
6. H. P. Gush, W. F. J. Hare, E. J. Allin, and H. L. Welsh, Can. J. Phys. **38**, 176 (1960).
7. H. M. Roder, G. E. Childs, R. D. McCarty, and P. E. Angerhofer, Survey of the Properties of the Hydrogen Isotopes Below Their Critical Temperatures, National Bureau of Standards Technical Note 641 (August 1973), Section 9.1.
8. G. N. Lewis and M. Randall, Thermodynamics, revised by K. S. Pitzer and L. Brewer (McGraw-Hill, New York, 1961), 2nd ed., pp. 595-600.
9. G. Herzberg, Molecular Spectra and Molecular Structure. I: Spectra of Diatomic Molecules (Van Nostrand Reinhold Co., New York, 1950), 2nd ed., p. 98, Eq. (III, 91).
10. Richard N. Dixon, Spectroscopy and Structure (John Wiley & Sons, New York, 1965), p. 83, Eq. 4.6.
11. Ref. 9, pp. 530-533.
12. Ref. 10, pp. 83-87.
13. Ref. 9, pp. 106-7, Eqs. (III-116, -121).
14. A. Crane and H. P. Gush, Can. J. Phys. **44**, 373 (1966).
15. A. Watanabe and H. L. Welsh, Can. J. Phys. **45**, 2859 (1967).
16. S. A. Boggs, M. J. Cloutier, and H. L. Welsh, Can. J. Phys. **50**, 2063 (1972).
17. A. R. W. McKellar, Can. J. Phys. **51**, 389 (1973).
18. A. R. W. McKellar and H. L. Welsh, Can. J. Phys. **52**, 1082 (1974).
19. E. W. Albers, P. Hartech, and R. R. Reeves, J. Amer. Chem. Soc. **86**, 204 (1964).
20. R. Frauenfelder, F. Heinrich, and J. B. Olin, Helv. Phys. Acta **38**, 279 (1965).
21. W. M. Jones, J. Chem. Phys. **17**, 1062 (1949).