ity. This system is also precise and allows fast analyses. When water miscible solvents, such as acetone, are optimum, it may be possible to employ salting-out techniques for phase separation (21).

References

1. J. Ruzicka and E.H. Hansen, Anal. Chim. Acta, *179*, 1 (1986).
2. E.H. Hansen, "Flow Injection Analysis," Thesis for Degree of Doctor Technices, Chemistry Dept. A, Technical University of Denmark, 1986, p. 57.
3. S. Greenfield, G.M. Hiefte, N. Omenetto, A. Scheeline, and W. Slavin, Anal. Chim. Acta, *180*, 69 (1986).
4. R.J. Henry, D.C. Cannon and J.W. Winkelman, "Clinical Chemistry, Principles and Techniques," Harper and Row: Hagerstown, MD, 1974, pp. 641-712.
5. G.D. Christian and F.J. Feldman, "Atomic Absorption Spectroscopy, Applications in Agriculture, Biology and Medicine," R.E. Krieger Publishing Co.: New York, 1979, p. 181.
6. M. Burguera and J.L. Burguera, Anal. Chim. Acta, *179*, 351 (1986).
7. S. Olsen, L.C.R. Pessenda, J. Ruzicka and E.H. Hansen, Analyst, *108*, 905 (1983).
8. O.F. Kamson and A. Townshend, Anal. Chim. Acta, *155*, 253 (1983).
9. F. Malamas, M. Bengtsson and G. Johannson, Anal. Chim. Acta, *160*, 1 (1984).
10. A.T. Haj-Hussein, G.D. Christian and J. Ruzicka, Anal. Chem., *58*, 38 (1986).
11. T.P. Lynch, N.J. Kernoghan and J.N. Wilson, Analyst, *109*, 839 (1984).
12. L. Nord and B. Karlberg, Anal. Chim. Acta, *145*, 151 (1983).
13. M. Silver, M. Gallego and M. Valcarcel, Anal. Chim. Acta, *179*, 341 (1986).
14. R.H. Atallah, Ph.D. Thesis, University of Washington, 1987.
15. A.S. Attiyat, A.S. and G.D. Christian, Clin. Chim. Acta, *137*, 151 (1984).
16. O. Menis and T.C. Rains, in "Analytical Flame Spectroscopy," R. Mavrodineanu, Ed., Springer-Verlag: New York, 1970, p. 63.
17. F.J. Feldman, R.E. Bosshart and G.D. Christian, Anal. Chem., *39*, 1175 (1967).
18. G.D. Christian and F.J. Feldman, Can. Spectrosc., *14*, 1 (1969).
19. A.S. Attiyat and G.D. Christian, Anal. Chem., *56*, 439 (1984).
20. A.S. Attiyat, J. Flow Injection Analysis, submitted for publication, 1986.
21. C.E. Matkovich and G.D. Christian, *Anal. Chem. 46*, 102 (1974).

Acknowledgements

The author gratefully acknowledges support of Yarmouk University, for this project and the technical assistance of Mr. Jamil Shatnawi.

Isotopic Mass Effects on the Spectroscopic Parameters of Diatomic Molecules

J. F. Ogilvie

Contribution from Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043

Received: July 6, 1987 Accepted: August 10, 1987

Résumé

La correction de la masse isotopique de Ross, Eng et Kildal (1974) est appliquée aux paramètres spectroscopiques mécaniques et électroniques de la molécule homonucléaire diatomique O_2. Les valeurs prédites de ces paramètres sont comparées aux résultats expérimentaux. Cette nouvelle application de la théorie s'avère généralement satisfaisante, mais certains résultats expérimentaux nécessiteront probablement une vérification expérimentale.

Abstract

The isotopic mass correction of Ross, Eng and Kildal (1974) is applied to the mechanical and electronic spectroscopic parameters of the homonuclear diatomic molecule O_2. Predictions of values of parameters are compared with experimental results. This extension of the theory is found to be generally satisfactory, but certain experimental results probably require remeasurement.

Introduction

Since the early days of molecular spectroscopy, there has been a great interest in the mass effects on molecular energies and on their energy differences which appear in spectroscopic transitions in absorption, emission or Raman scattering. The procedure of Born and Oppenheimer (1) provided a theoretical basis for not only the dominant mass effects in spectroscopic parameters, due to nuclear motion, but also the effects of the coupling of electronic and nuclear motions that lead to deviations from the limiting behaviour according to the first (or zero-order) approximation. Because of both the relative simplicity of the spectra of diatomic molecules and the relative ease of application of theoretical treatments of the electronic and nuclear motions and of the analysis of the molecular spectra, these molecules have fruitfully served as convenient tests of both theories and theoretical methods. Already at the time of Dunham's (2) work on a quantitative treatment of rotational and vibrational energies in diatomic molecules in $^1\Sigma$ electronic states, the principal mass factor in the corresponding spectroscopic parameters was understood, and the spectra of isotopic species of the same chemical substance were successfully analyzed on that basis (3). However, during the course of time in which spectra were measured with ever increasing spectral resolution, and a concomitant increase of the precision of the transition wavenumbers (or frequencies), significant discrepancies appeared between the measured wavenumbers and those predicted on the basis of the simple factor embodied in the reduced mass of the isotopic species. In 1974, Ross *et al.* (4) discovered an empirical correction to the Dunham formula that successfully accounted for the isotopic mass effects within the accuracy of their measurements. Later, this formulation was given a theoretical justification (5,6). Since that time, this formulation has been applied to many heteronuclear diatomic molecules in $^1\Sigma$ electronic states and to several vibration-rotational parameters for which the mass coefficients could be significantly determined. However, there has been little or no application to either homonuclear molecules or to other parameters describing the effects arising from the coupling of molecular rotational angular momentum with net spin or orbital angular momentum (in states other than $^1\Sigma$) that lead to further branches of lines in vibration-rotational spectra beyond the simple P and R branches of each vibration-rotational band of a molecule like $^{12}C^{16}O$ (4). In this paper, we discuss these topics and provide examples of their application to O_2 in its ground $^3\Sigma_g^-$ electronic state.

Treatment and Results

For the vibration-rotational energies (expressed in wavenumber units) of a particular isotopic variant of a diatomic molecule in a particular $^1\Sigma$ state, Dunham (2) developed the relation

$$E(v,J) = \sum_{k=0} \sum_{l=0} Y_{kl} (v + 1/2)^k [J(J + 1)]^l \quad [1]$$

in which the coefficients Y_{kl} of the powers of the functions of the vibrational v and rotational J quantum numbers incorporate a dependence on the reduced mass $\mu = M_a M_b/(M_a + M_b)$ calculated from the masses M_a and M_b of the neutral atoms that are the products of dissociation of the molecule in that electronic state. The relation developed by Ross et al. (4) for each Y_{kl} is

$$Y_{kl} = U_{kl} \mu^{-(k+2l)/2} [1 + m_e(\Delta^a_{kl}/M_a + \Delta^b_{kl}/M_b)] \quad [2]$$

in which all the mass dependence of the term-value coefficients Y_{kl} is taken into account (within present experimental error) by the evident mass factors so that the parameters U_{kl} and the two Δ_{kl} are formally independent of mass for a particular chemical species in a specific electronic state. In a homonuclear diatomic molecule, the equal nuclear charges of the two nuclei implies that the simplification

$$Y_{kl} = U_{kl} \mu^{-(k+2l)/2} [1 + m_e \Delta_{kl}/\mu] \quad [3]$$

is achieved such that only a single Δ_{kl} parameter exists for a given couple k and l.

One can then apply this well established formula to the various parameters Y_{kl} of the vibration-rotational spectra of O_2. From the far infrared spectrum of $^{16}O_2$ (7) (magnetic-dipole transitions) and from the laser-magnetic-resonance (8) and microwave (9,10) spectra of $^{16}O_2$ and $^{18}O_2$, the values of some parameters have been accurately determined (11); the parameters of interest are collected in Table I.

First of all, using the values of the equilibrium rotational parameter B_e for the latter isotopic variants of

Table I. Equilibrium spectroscopic parameters $/m^{-1}$ of $^{16}O_2$ and $^{18}O_2$ and their dependence on reduced mass.

quantity	dependence	$^{16}O_2$	$^{18}O_2$
B_e	μ^{-1}	144.538270±.00013	128.463315±.00017
α_e	$\mu^{-3/2}$	1.58126 ±.00027	1.32472 ±.00017
$D_e/10^{-4}$	μ^{-2}	4.850 ±.033	3.936 ±.17
λ_e	μ^0	198.233739±.000067	198.233526±.00002
γ_e	μ^{-1}	$-0.8415282 \pm 6.7 \times 10^{-6}$	$-0.7477976 \pm 1.0 \times 10^{-5}$

Table II. Derived mass-independent molecular parameters of O_2.

$U_{0,1}$	1156.259402 $m^{-1}amu$	$U_{1,1}$	-35.79328 m^{-1} $amu^{3/2}$
$\Delta_{0,1}$	-2.0373	$\Delta_{1,1}$	-13.04
R_e^{BO}	$(1.20745409\times10^{-10}\pm3\times10^{-18})$ m		

O_2 and the eq. 3 above, one can derive values of the mass-independent quantities $U_{0,1}$ and $\Delta_{0,1}$. Then one can use the latter quantities in turn to predict the equilibrium rotational parameters of any other isotopic variant of O_2. A more interesting procedure is to use the values of the equilibrium (first) vibration-rotation interaction parameter α_e in Table I to derive the values of the quantities $U_{1,1}$ and $\Delta_{1,1}$. With the combination of these data from B_e and α_e, listed in Table II, one can predict values ±.0002 m^{-1} of the rotational parameter B_0 for the ground vibrational state of any isotopic variant of O_2 for a more direct comparison, presented in Table III, with experimental results from investigations of Raman scattering.

Because the same kinds of adiabatic and nonadiabatic effects that affect the accuracy of the Born-Oppenheimer approximation for the 'mechanical' spectroscopic paramaters Y_{kl} also affect the electronic parameters, it should be possible to apply eq. 3 also to the electronic parameters such as the spin-spin λ and the spin-rotation γ interaction coefficients. Again, one can then proceed to predict some values for the ground vibrational state of some isotopic species, but in this case fewer experimental data are available for comparison. Such a comparison is possible however for $^{16}O^{18}O$; the predicted values (m^{-1}) ±.00007 of λ_0 and ±0.000012 of γ_0 are compared with the respective experimental values in Table III. Other quantities can equally well be predicted by the same method, but accurate experimental data are not yet available for comparison.

Discussion and Conclusions

The data in Table III clearly demonstrate that it is possible to calculate the spectroscopic parameters, and in particular the rotational parameter B_0, more accurately than they can be measured by means of Raman scattering. Of course, it is only fair to state that the data in Table 1 were derived from experiments in millimetre-wave and far infrared spectroscopy (the latter using either the method of laser magnetic resonance or laser sources), in both cases with the great accuracy commonly associated with microwave measurements. It is noteworthy, however, that the Raman measurements of B_0 of $^{17}O_2$, and even of $^{16}O_2$ itself (for which a pure sample is easily obtained), deviate significantly from the predicted values.

Table III. Comparison of predicted and experimentat spectroscopic parameters /m^{-1} the ground vibrational states of isotopic O_2 molecules.

quantity	species	predicted	measured	reference
B_0	$^{16}O^{16}O$	143.7676	143.777±.003	12
B_0	$^{16}O^{17}O$	139.5330	139.538±.005	13
B_0	$^{16}O^{18}O$	135.7853	135.781±.008	14
B_0	$^{17}O^{17}O$	135.2980	135.314±.004	12
B_0	$^{17}O^{18}O$	131.5497	131.546±.002	12
B_0	$^{18}O^{18}O$	127.8009	127.796±.004	12
λ_0	$^{16}O^{18}O$	198.467429	198.467625±0.00014	15
γ_0	$^{16}O^{18}O$	-0.7955979	-0.7955103±.000023	15

The molecular parameter $U_{0,1}$ is directly related to the mass-independent (Born-Oppenheimer) equilibrium internuclear separation R_e^{BO}. The inaccuracy of this quantity indicated in Table II has propagated only from nominal experimental errors of measurement of frequency. In fact, the contribution to the true error from the uncertainty in the fundamental physical constants (16) (specifically the Planck and Avogadro constants) is larger, ~10^{-17} m. However, an even larger contribution to the uncertainty results from the model by means of which the data in Table I were derived from experimental data, specifically from the values of the pertinent spectroscopic parameters for the two isotopic variants of O_2 in only the two vibrational states $v=0$ and $v=1$. If the deficiency of this model is taken into account, then the uncertainty of the determination of R_e^{BO} is probably of the order of 10^{-16} m, still much smaller than the nuclear diameters. It should be noted that this quantity R_e^{BO} has a well defined meaning, both theoretically and experimentally (through $U_{0,1}$), unlike the value of the "weighted mean" internuclear separation $(1.20754 \pm 0.00001)\times10^{-10}$ m derived from the Raman results (12) (of which even the experimental basis is suspect, as already pointed out).

Although the agreement between the predicted and measured values of λ_0 in Table III is fair, the agreement in the case of γ_0 is worse. The value 198.467398 m^{-1} predicted (11) for λ_0 by a different method is in somewhat worse agreement than the value in Table III; the value -0.7955947 m^{-1} predicted (11) for γ_0 is in poor agreement with the experimental value but

Table IV. Spectroscopic and potential-energy parameters of $^{16}O_2$.

	/m^{-1}			
ν_{1-0}	155639.934	±0.2	a_1	-3.01025
ω_e	157995.54	±1.6	a_2	5.87965
B_e	144.56228	±0.0013	a_3	-7.8773
α_e	1.59537	±0.31	a_4	-0.5585
$D_e/10^{-4}$	4.71	±0.1		
a_0	43169267	±87		

similar to the prediction in Table III. Mizushima (11) commented that measurement of more lines with greater precision is planned in order to seek improvement of the experimental data so as provide a better test of the theoretical predictions. Again the measurements in vibrational states beyond v = 1 would be desirable to test the linear model for the treatment of the experimental data.

As a means of illustrating the effects of the linear model for the spectroscopic parameters, the data in Table IV represent the values of some parameters that may be compared with those in the previous tables. A previous compilation (17) of vibrational energies, rotational and centrifugal distortion parameters may be used to derive equilibrium values of quantities for comparison; these data were supplanted by more recent and accurate data wherever possible. The origin ν_{1-0} of the fundamental band of $^{16}O_2$ was newly determined from the combination of the accurate rotational parameters (9,10) for the combining states v = 0 and v = 1, with the precise measurements of the few vibration-rotational absorption lines in the electric quadrupole spectrum (18). Then fitting all these data for the vibrational states up to v = 28 generated the results in Table IV, and their further use according to the Dunham (2) formalism produced the potential-energy parameters a_j.

It is clear from the comparison of different values of α_e and D_e of $^{16}O_2$ in Tables I and IV that the linear model (necessitated by the lack of precise microwave or laser measurements beyond v = 1) may lead to precise but inaccurate values of these quantities. For instance, such a large magnitude of $\Delta_{1,1}$ in Table II is probably due to the linear model. The comparison of B_e values in Tables I and IV is however inappropriate because the Dunham correction (the distinction between $Y_{0,1}$ and B_e) has been applied to the result in Table IV. However the value of B_e in Table IV may be used, with the value $g_n = 0.000125 \pm 8 \times 10^{-6}$ (19), to estimate the adiabatic equilibrium internuclear separation of $^{16}O_2$; the result if $(1.207597 \pm .000005) \times 10^{-10}$ m, significantly different (as expected) from the Born-Oppenheimer separation given in Table II. The acquisition of more accurate spectroscopic data for the many vibrational states of the ground electronic state of O_2 is clearly desirable, because the accuracy of many existing data (17) of this important chemical species fall far short of what is attainable by modern techniques (20); at the same time data of $^{18}O_2$ of comparable modern accuracy would enable a much improved determination of the molecular properties that being independent of mass reflect accurately the electronic distribution of the relatively isolated ground electronic state. The above results demonstrate that for a homonuclear diatomic molecule the mass dependence of not only the mechanical spectroscopic parameters Y_{kl} but also the electronic parameters such as λ and γ may be adequately taken into account by means of equation [2] due to Ross et al. (4).

Acknowledgment

I am grateful to Professor M. Mizushima for providing preprints of results.

References

1. M. Born and J.R. Oppenheimer, Ann. Phys. Leipzig, *84*, 457 (1927).
2. J.L. Dunham, Phys. Rev., *41*, 721 (1932).
3. I. Sandeman, Proc. Roy. Soc. Edinburgh, *60*, 210 (1940).
4. A.H.M. Ross, R.E. Eng and H. Kildal, Opt. Commun., *12*, 433 (1974).
5. P.R. Bunker, J. Mol. Spectrosc., *68*, 367 (1977).
6. J.K.G. Watson, J. Mol. Spectrosc., *80*, 411 (1980).
7. L.R. Zink and M. Mizushima, J. Mol. Spectrosc., in press (1987).
8. M. Mizushima, L.R. Zink and K.M. Evenson, J. Mol. Spectrosc., *107*, 395 (1984).
9. Y. Endo and M. Mizushima, Jap. J. Appl. Phys., *21*, L379 (1982).
10. Y. Endo and M. Mizushima, Jap. J. Appl. Phys., *22*, L534 (1983).
11. M. Mizushima, Jap. J. Appl. Phys., *26*, 645 (1987).
12. H.G.M. Edwards, D.A. Long, K.A.B. Najm and M. Thomsen, J. Raman Spectrosc., *10*, 60 (1980).
13. H.G.M. Edwards, D.W. Farwell, D.A. Long and K.A.B. Najm, Ind. J. Pure Appl. Phys., *16*, 354 (1978).
14. H.G.M. Edwards, E.A.M. Good and D.A. Long, J. Chem. Soc. Faraday Trans. II, *72*, 865 (1976).
15. W. Steinbach and W. Gordy, Phys. Rev., *All*, 729 (1975).
16. E.R. Cohen and B.N. Taylor, CODATA Bull. No. 63 (1986).
17. D.M. Creek and R.W. Nicholls, Proc. Roy. Soc. London, *A341*, 517 (1976).
18. J. Reid, R.L. Sinclair, A.M. Robinson and A.R.W. McKellar, Phys. Rev., *A24*, 19444 (1981).
19. K.M. Evenson and M. Mizushima, Phys. Rev. *A6*, 2197 (1972).
20. R.A. Copeland, P.C. Cosby, D.R. Crosley, J.B. Jeffries and R.E. Slanger, J. Chem. Phys., *85*, 2500 (1987).