# Adiabatic and Nonadiabatic Effects in the Vibration-rotational Spectra of Carbon Oxide CO X $^{1}\Sigma^{+}$

J. F. Ogilvie\* and M. C. C. Ho Institute of Atomic and Molecular Sciences, Academia Sinica, P. 0. Box 23-166, Taipei, Taiwan' 106, R.O.C. (Received July 27, 1993)

Within the Born-Oppenheimer approximation of separate treatment of electronic and nuclear motions, 27 independent coefficients of radial functions have been evaluated to represent the internuclear potential energy and for the complementary adiabatic and nonadiabatic rotational effects of CO in the electronic ground state X  ${}^{1}\Sigma^{+}$ . These parameters reproduce the frequencies and wavenumbers of about 20000 lines of pure rotational and vibration-rotational transitions within approximately the uncertainty of their measurement. The specific contributions of potential energy, adiabatic and nonadiabatic rotational effects to the coefficient of the term [J(J+1)] in the vibrationrotational energy are delineated, and the relative magnitudes of other contributions to a few terms are discussed. The currently most accurate value of the equilibrium internuclear distance is  $R_{e}/10^{-10}$  m = 1.12822933 ± 0.00000096.

### I. INTRODUCTION

Being the most stable electrically neutral diatomic molecule, carbon oxide is found in both interstellar clouds at temperatures about 10 K and the outer atmospheres of the sun and other stars at temperatures exceeding 5000 K. In terrestrial environments it is both a product of incomplete combustion of fuels containing carbon and an intermediate species in these combustion processes. A powerful laser system based on vibration-rotational transitions of CO has scientific and technological applications. In all these cases this molecular species has been detected by means of optical spectra, the pure rotational lines in the microwave and far infrared regions and the vibration-rotational lines in the mid and near infrared regions in both absorption and emission, whereas much less commonly by means of **Raman** scattering and electronic transitions in various spectral regions. Although the nuclides <sup>12</sup>C and <sup>16</sup>O are predominant in all known environments, spectra of less abundant isotopic variants have been well measured, of molecules containing not only the stable nuclides <sup>13</sup>C, <sup>17</sup>O and <sup>18</sup>O but also the radioactive nuclide <sup>14</sup>C. The collection of all these

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spectral data involving transitions even within the electronic ground state X  ${}^{1}\Sigma^{+}$  numbers so many thousands of distinct lines that their representation in a compact and physically meaningful form presents a formidable challenge to spectroscopists.

In order to take into account in a comprehensive and systematic manner all the vibration-rotational spectral data of multiple isotopic variants of a particular diatomic molecule in the electronic state  ${}^{1}\Sigma$ , one must understand all the sources of the dependence on nuclear mass. Since the development of molecular spectroscopy, the major effects of nuclear mass are recognised to be incorporated in the factor the reduced mass  $\mu \equiv M_a M_b / (M_a + M_b)$ , in which  $M_a$  and  $M_b$  are respectively the masses of the neutral atoms A and B into which the (neutral) molecule dissociates. Before the work of van Vleck [1] slight deficiencies of this model relative to experimental error of measurement of wavenumbers of spectral lines were known, but he delineated the adiabatic and nonadiabatic effects. After Kratzer's application of a potential-energy function [2] in relation to vibration-rotational spectra, this function and the associated classical ideas of molecular structure were introduced into quantum mechanics by Born and Oppenheimer [3]: the total energy of the electrons and the coulombic repulsion between the nuclei relatively fixed in position act as a potential energy for the motion of the nuclei. The mechanical effects hence arise from the vibration and rotation of two atomic nuclei with their accompanying electrons relative to the centre of mass. Beyond these mechanical effects the adiabatic and nonadiabatic effects take into account the fact that the electrons follow imperfectly the nuclei in their vibrational and rotational motions; the detection of these effects indicates the limits of applicability of the treatment of Born and Oppenheimer that has been always understood to be approximate. The adiabatic effects signify that the (adiabatic) potential energy depends on not only the relative separation of the nuclei but also their relative momenta, hence the masses of the individual nuclei. The nonadiabatic effects take into account that the vibrational and rotational motions of the nuclei induce interactions with other electronic states. Because the only quantities formally observable are the total angular momentum and the energy, these adiabatic and nonadiabatic effects are artefacts resulting from the supposition of isolated electronic states and the separation of electronic and nuclear motions. However, within the conventional paradigm of distinct electronic states, the nonadiabatic vibrational interactions that result from the inertia of the electrons as the nuclei vibrate operate between electronic states of the same symmetry species, whereas the nonadiabatic rotational interactions operate between electronic states of electronic orbital angular momentum that differ by one unit. If the atoms have distinct atomic numbers, all these effects obviously depend on the masses of the individual nuclei, not merely the reduced mass. Therefore beyond the potential energy that is rigorously independent of nuclear mass according to the treatment of Born and Oppenheimer, three effects appear to apply for nuclei of each

atomic number, namely adiabatic, nonadiabatic vibrational and nonadiabatic rotational. Spectral data consisting of only frequencies (or wavenumbers) of lines in the absence of external fields exhibit the effects of only two variable quantities for the nucleus of each type, the nuclear mass (isotopic effect) and the additional rotational dependence. For this reason in order to separate these three extra-mechanical effects, in practice if not in principle we require further spectral information. The Zeeman effect enables the determination of the rotational magnetogyric ratio, the ratio of the rotational angular momentum to the magnetic dipolar moment; the rotational g factor (an expectation value of a particular vibrationrotational state) and its rotational and vibrational dependences yield separately the radial functions associated with the nonadiabatic rotational effects. For that reason, within the Born-Oppenheimer approximation, the nonadiabatic rotational effects have a closer relation to physical observables than the adiabatic and nonadiabatic vibrational effects for which there are no direct relations to measurable physical properties. With the knowledge of the nonadiabatic rotational effects from adequate Zeeman measurements we can in principle generate the remaining functions. As these rotational and vibrational dependences of  $g_J$ have been determined experimentally for exceedingly few molecules, and are difficult to calculate accurately by means of purely theoretical methods, we must at present accept that the complete separation of these effects is generally impracticable. The most compact and physically meaningful representation of the vibration-rotational energies (or terms in wavenumber units), and the differences between them that constitute the wavenumbers of spectral lines, is made currently in terms of coefficients in the radial functions for the potential energy and the additional effects just described.

During the course of time we have developed methods, based on the analytic approach within the Born-Oppenheimer separation of electronic and nuclear motions that Dunham developed [4] and that has since been greatly extended, to invert spectral data to yield successively the potential-energy function [5], the adiabatic effects [6] and the nonadiabatic rotational effects [7]. The theory to take into account explicitly the nonadiabatic vibrational effects has been developed [8], and remains to be applied to the extent practicable according to the inevitably limited quantity and quality of spectral data of a particular diatomic molecular species. In the present work we have applied in particular our theoretical results [8] to reduce the abundant vibration-rotational data of carbon oxide CO in its electronic ground state X  ${}^{1}\Sigma^{+}$  to the coefficients of the radial functions; in so doing we have been able to deduce for the first time the relative importance of adiabatic and nonadiabatic effects in relation to some observable molecular properties.

# **II. PRINCIPLES OF THE METHOD**

As a function of the internuclear separation R the effective hamiltonian that is the

basis of our formulation is [8]

$$\mathcal{H}_{eff} = -\frac{\hbar^2}{2\mu} \frac{d}{dR} [1 + \beta(R)] \frac{d}{dR} + V^{BO}(R) + V^{ad}(R) + \frac{\hbar^2}{2\mu R^2} [1 \quad \mathbf{t} \quad \alpha(R)] J(J+1)$$

$$(1)$$

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that includes the operator  $[-\hbar^2/(2\mu)]d^2/dR^2$  for the kinetic energy of the nuclei with their reduced mass  $\mu$ , the potential energy  $V^{BO}(\mathbf{R})$  that is formally independent of nuclear mass, the term  $\hbar^2 J(J+1)/(2\mu R^2)$  for the centrifugal nuclear motion, the adiabatic term  $V^{ad}(R)$ , the nonadiabatic rotational term  $\alpha(R)$  and the nonadiabatic vibrational term  $\beta(R)$ . Hereafter we assume units of wavenumbers for all quantities of energies according to conventional spectral usage. The reduced variable z for internuclear distance [9,10]

$$z \equiv 2(R - R_e)/(R + R_e) \tag{2}$$

as argument in the functions

$$V^{ad}(R) \longrightarrow m_e \left( \sum_{j=1} u_j^a z^j / M_a + \sum_{j=1} u_j^b z^j / M_b \right)$$
(3)

$$\alpha(R) \longrightarrow m_e \left( \sum_{j=0} t_j^a z^j / M_a + \sum_{j=0} t_j^b z^j / M_b \right)$$
(4)

$$\beta(R) \longrightarrow m_e \left( \sum_{j=0} s_j^a z^j / M_a + \sum_{j=0} s_j^b z^j / M_b \right)$$
(5)

facilitates practical applications to represent the extra-mechanical effects that each contain the ratio of electronic to nuclear masses; this property enables us to consider these functions to act as small perturbations of the potential energy

$$\boldsymbol{V}(\boldsymbol{Z}) = c_0 z^2 \left( 1 \quad \mathbf{t} \quad \sum_{j=1} c_j z^j \right) \tag{6}$$

that exerts the dominant influence on the spectral terms. To avoid problems with the asymptotic behaviour of a polynomial form of  $\beta(R)$  in Eq. (1), we carried this function in its symbolic form through all calculations [8] until the last stage.

The eigenvalues (or terms in wavenumber units) of this hamiltonian take the form of a double summation of series in the functionals  $v + \frac{1}{2}$  and J(J + 1), involving respectively the vibrational quantum number v and the rotational quantum number J (in the absence of other significant sources of angular momentum in the molecule), to non-negative powers [7]:

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$$E_{vJ} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} (Y_{kl} + Z_{kl}^{v,a} + Z_{kl}^{v,b} + Z_{kl}^{r,a} + Z_{kl}^{r,b}) \left(v + \frac{1}{2}\right)^{k} (J^{2} + J)^{l}$$
(7)

here the explicit isotopic dependences of the terms  $E_{vJ}$  and the term coefficients  $Y_{kl}$  and various  $Z_{kl}$  have been suppressed. The coefficients  $Y_{kl}$  that result from the potential-energy function V(z) and the centrifugal motion of the nuclei are functions of the coefficients  $c_i$ , the reduced mass  $\mu$  of the particular isotopic variant, the equilibrium internuclear distance  $R_e$  and the equilibrium force coefficient  $k_e$ , or equivalently the harmonic vibrational parameter  $\omega_e = (k_e/\mu)^{\frac{1}{2}}/(2\pi c)$  and the equilibrium rotational parameter  $B_e = h/(8\pi^2 c \mu R_e^2)$ ;  $c_0 = \frac{1}{4}\omega_e^2/B_e = k_e R_e^2/(2ch)$ . The coefficients  $Z_{kl}^{\nu}$  of separately each nucleus a and b that take into account the vibration-rotational ramifications of the putative adiabatic and nonadiabatic vibrational effects are functions of not only the coefficients  $u_i^{a,b}$  and  $s_i^{a,b}$  but also the parameters within the expressions  $Y_{kl}$ , whereas the corresponding coefficients  $Z_{kl}^r$  that take into account analogously the extra rotational consequences [8] of the nonadiabatic vibrational and rotational effects contain the coefficients  $s_j^{a,b}$  and  $t_j^{a,b}$  and the parameters within  $Y_{kl}$ . These expressions of  $Y_{kl}$  and various  $Z_{kl}$  were generated by means of symbolic computation (computations done separately with Maple and Reduce for verification) with the application of hypervirial perturbation theory [8,11] and then converted for use with the variable z. Analytic expressions of the coefficients  $Y_{kl}$  containing parameters  $c_j$  up to j = 10 have been published in machine-readable form [12], and additional expressions containing  $c_j$  up to j = 24 are being made available with ample expressions likewise for  $Z_{kl}^{v}$ and  $Z_{kl}^r$  and their derivatives with respect to the parameters. The latter expressions contain for each nucleus the ratio  $m_e/M$  of electronic rest mass to an atomic mass; terms in the hamiltonian that lead to this ratio appearing to a power greater than unity in terms in the eigenvalues or terms have been omitted because such contributions are negligible relative to existing levels of error of frequency measurements. For the same reason we use atomic masses instead of nuclear masses because the latter are generally inaccurately known and the differences between the two sets of masses are negligible in relation to experimental error.

An alternative equation to fit the spectral terms

$$E_{vJ} = \sum_{k=0} \sum_{l=0} U_{kl} \mu^{\frac{1}{2}k+l} [1 + m_e (\Delta_{kl}^a / M_a + \Delta_{kl}^b / M_b)] \left(v + \frac{1}{2}\right)^k (J^2 + J)^l$$
(8)

contains the purely empirical parameters  $U_{kl}$  and  $\Delta_{kl}^{a,b}$  that are formally independent of nuclear mass. The correct application of this equation requires that constraints be imposed [13,14] on the coefficients  $U_{kl}$  so that essentially the coefficients  $U_{kl}$ , l > 1, become defined in terms of the coefficients  $U_{k,0}$  and  $U_{k,1}$ ; the corresponding relations between the coefficients  $\Delta_{kl}^{a,b}$  are necessarily founded less rigorously [15].

We applied the method of estimation of nonlinear parameters [7] to evaluate the

applicable coefficients of the radial functions in Eqs. (3)-(6) from the frequencies and wavenumbers of pure rotational and vibration-rotational spectral lines that are the difference of two terms  $E_{vJ}$ . Because of the nonlinear dependence of the coefficients  $c_j$ , although the coefficients in Eqs. (3)-(5) occur only linearly, the procedure is iterative, and the criterion of the best fit is that the sum of the squares of the residuals between the experimental and calculated wavenumbers is a minimum. The algorithm employs analytic expressions of not only the term coefficients  $Y_{kl}$  and various  $Z_{kl}$  but also their derivatives with respect to the parameters [12]; standard statistical tests are implemented.

# III. APPLICATION TO CO

Spectral data consisting of frequencies and wavenumbers of pure rotational and vibration-rotational transitions of CO are numerous. The largest sets of data included vibration-rotational transitions, about 11000 lines by Guelachvili and coworkers [16-18], with which we combined a further 7000 lines from solar spectra [19] and about 750 lines of <sup>14</sup>C<sup>16</sup>O[20], with other smaller sets of data listed by Farrenq et al. [19] and pure rotational lines in the microwave [21,22] and far infrared regions [23-26]. The data in the collection reported before 1985 include many duplicated lines; a preliminary fit of these data with some more recent pure rotational data enabled the pruning of about 4000 duplicate lines of relatively larger uncertainties than the ones retained. When the solar data and other sets were added, further duplication of transitions arose; because the uncertainties of many lines were comparable and because the values resulted from independent measurements, almost all the lines except a few obvious outliers were retained. The collection of lines in the final fit numbered 16890, consisting of 48 pure rotational and 10880 vibration-rotational lines of  $^{12}C^{16}O$  up to v = 41 and J = 133 in the sequences  $\Delta v = 1, 2$  and 3, 1 rotational and 62 vibration-rotational lines of  ${}^{12}C^{17}O$  up to v = 1, 36 rotational and 1131 vibration-rotational lines of <sup>12</sup>C<sup>18</sup>O, 20 rotational and 3264 vibration-rotational lines of <sup>13</sup>C<sup>16</sup>O, 34 vibrationrotational lines of <sup>13</sup>C<sup>17</sup>O, 1 rotational and 655 vibration-rotational lines of <sup>13</sup>C<sup>18</sup>O, and 1 rotational and 757 vibration-rotational lines of <sup>14</sup>C<sup>16</sup>O, including 4572 duplicated lines in total; further details of the composition of the data sets are found in the original papers. To each line was assigned an estimated uncertainty of its absolute accuracy; these values were generally those indicated by the authors of the reported data, tempered by factors drawn from experience of either preliminary fits or fits of partial sets of data. Exceptions were made for individual lines that deviated markedly from the calculated values in later fits, in which case the uncertainty was increased to diminish the effect on the fit. The weight of each datum in the fit was the reciprocal square of the associated uncertainty.

# IV. RESULTS

The values of the parameters resulting from the best fit of the 16890 lines appear in Table I. Therein the values of  $t_0^{C,O}$  were constrained to reproduce the rotational g factor  $g_J \equiv (0, 1|g_J|0, 1)$  of the isotopic variants for which measurements are available [21], accord\_ ing to the partition of this factor between the two nuclei [27]; this constraint was imposed because experience from attempts to fit these coefficients by means of only measurements of wavenumbers of spectral lines measured in the absence of applied fields resulted in poorly determined values and large correlations with  $R_e$  or  $U_{0,1}$ . The values of the remaining 26 independent parameters are those from the best fit according to the criterion of the Fstatistic that takes into account not only the sum of the squared residuals but also the number of degrees of freedom (the number of data minus the number of fitted parameters). That the normalised standard deviation of the fit appears to be significantly less than unity indicates that the uncertainties of many data, particularly those of Guelachvili and coworkers [16-18], were conservatively estimated. The magnitudes of correlation coefficients from the variance-covariance matrix were generally satisfactorily less than unity except notably between the parameters  $c_1$  and  $c_2$ ,  $u_1^C$  and  $u_2^C$ ,  $u_3^C$  and  $u_4^C$ , and  $u_1^O$  and  $u_2^O$ ; except for the large magnitude of correlation between  $c_1$  and  $c_2$  that is atypical and that arose despite the relatively small standard errors of these parameters, this behaviour is typical of fits to such sets of parameters of various molecules tested in the present project. Thus despite the only moderate ratios of magnitudes of the potential-energy coefficients  $c_j$  to the corresponding estimated standard errors for j > 4, these values appear reasonably independently determined; all these parameters  $c_j$ ,  $0 \le j \le 16$ , are evidently required, as fits involving less extensive sets yielded much larger normalised standard deviations. Without exception the parameters  $u_i^{C,O}$  and  $t_1^C$  are well defined in relation to their corresponding standard errors despite the nominally large correlations between some pairs of  $u_j^{C,O}$ ; because these large magnitudes of correlation coefficients are found in almost all cases between parameters having small standard errors, these magnitudes are acceptable. Excessive parameters in any radial function yielded, in addition to a decreased value of the F statistic, both relatively large standard errors and large correlation coefficients that proved these parameters to be statistically' insignificant. Because of lack of experimental data to enable the coefficients  $s_j^{C,O}$  to be evaluated, these values were constrained to zero; the values of  $t_j^{C,O}$  with j > 0 and of  $u_j^{C,O}$  with j > 1 in Table I are only effective values according to that condition. The maximum range of validity of the various radial functions is indicated in the table.

Based on the results in the table and the expressions of the term coefficients, we evaluated the various contributions for  ${}^{12}C^{16}O$  of the total coefficient of  $(v + \frac{1}{2})^k [J(J t 1)]^l$  for a few sets of values of k and l of particular interest; for all quantities  $Y_{kl}$  and  $Z_{kl}$  here the SI units  $m^{-1}$  are applicable. For k = 0 and l = 1,  $Y_{0,1}^{(0)} = B_e = 193.160249$  with its estimated

j	cj	$t_j^C$	$t_j^O$	$u_j^C / 10^6 \text{ m}^{-1}$	$u_j^O/10^6 { m m}^{-1}$
0	$(60931428.57 \pm 9.1) \text{ m}^{-1}$	[-1.8511	[-1.8061		
1	-1.6966778 f0.0000057	$0.2844 \pm 0.0042$		-11.023 f0.186	- 18.66 f0.37
2	1.209061 f0.000021			127.82 f0.66	54.34 f1.33
3	-0.501156 f0.00021			-316.31 f6.9	156.2 f5.3
4	0.30831 f0.00133			500.3 f35.8	
5	0.03372 f0.0054				
6	$-0.7436 \pm 0.067$				
7	0.4089 f0.114				
8	7.326 f1.21				
9	$^{-40.32}_{\pm 6.3}$				
10	64.25 f9.4	$U_{1,0} = (568135.029 \pm 0.025) \text{ m}^{-1} u^{\frac{1}{2}}$			
11	$172.30 \pm 54.2$	$U_{0,1} = (1324.34697 + 0.00031) \text{ m}^{-1}u$ $k_e = (1901.75106 \pm 0.00113)N \text{ m}^{-1}$ $R_e = (1.12822933 \pm 0.00000096) \times 10^{-10} \text{ m}$			
12	-1206 f285				
13	3885 f770	range of validity $0.86 \leq R/10^{-10} \text{m} \leq 1.60$			
14	- 10230 f1400				
15	$\begin{array}{r} 25560 \\ \pm 4500 \end{array}$				
16	-58350 f20000				

TABLE I. Cefficients of the radial functions and other properties of the diatomic molecule CO in the state  $X\,{}^1\Sigma^+$ 

\* The normalised standard deviation of the fit was 0.55 and the F-value was 1.65  $\times 10^{18}$  for 16890 lines,  $0 \le v \le 41$ ,  $0 \le J \le 133$ , and for isotopic variants  ${}^{12,13,14}C^{16,17,18}O$  in various combinations. Brackets [] indicate constrained values.

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standard error  $\pm \delta Y_{0,1}^{(0)} = 0.000047$  and  $Y_{0,1}^{(2)} = -0.000226$ ; although the latter magnitude is significant relative to the experimental error  $\delta Y_{0,1}^{(0)}$  the subsequent Dunham correction  $Y_{0,1}^{(4)}$ (that contains an additional factor  $\gamma^2 \equiv (2B_e/\omega_e)^2 \sim 3.2 \times 10^{-6}$ ) is entirely negligible. The term coefficients pertaining purely to the nonadiabatic rotational effects [8] have the values  $Z_{0,1}^{r,C} = -0.01634 \pm 0.00006$  and  $Z_{0,1}^{r,O} = -0.01196 \pm 0.00006$  respectively; these magnitudes are much larger than both the experimental error  $\delta Y_{0,1}^{(0)}$  and the Dunham correction  $Y_{0,1}^{(2)}$ . The term coefficients pertaining purely to the adiabatic vibrational effects have the values  $Z_{0,1}^{v,C} = -0.0015975$  and  $Z_{0,1}^{v,O} = -0.002029$ , of which the magnitudes are also much larger than those of both the experimental error  $\delta Y_{0,1}^{(0)}$  and Dunham correction, but smaller than those of the the nonadiabatic rotational effects. The latter feature contrasts with the case k = 0 and l = 1 for <sup>1</sup>H<sup>35</sup>Cl for which the nonadiabatic rotational and adiabatic effects had comparable magnitudes; for HCl the magnitudes of the Dunham corrections  $Y_{kl}^{(2)}$  were generally much larger than the experimental errors  $\delta Y_{k,l}^{(0)}$  for several sets of k and 1.

For other combinations of k and I, the nonadiabatic vibrational effects remain at present inextricably intertwined with the adiabatic effects in the coefficients  $Z_{kl}^{v}$  or with the nonadiabatic rotational effects in the coefficients  $Z_{kl}^r$  of the individual nuclei. However comparisons of available magnitudes remain meaningful. In the case of the principal coefficient for centrifugal distortion,  $Y_{0,2}^{(0)} = -6.123422 \times 10^{-4}, \delta Y_{0,2}^{(0)} = f8.5 \times 10^{-10}$  and  $Y_{0,2}^{(2)} = -2.1567 \times 10^{10}$ ; the magnitude of the experimental error here exceeds that of even the first Dunham correction. The associated rotational effects are  $Z_{0,2}^{r,C} = 1.116 \times 10^{-7}$ and  $Z_{0,2,-}^{r,O} = 0.7586 \times 10^{-7}$ , whereas the corresponding vibrational effects and  $Z_{0,2}^{v,C} = 0.5596 \times 10^{-7}$  and  $Z_{0,2}^{v,O} = 0.1522 \times 10^{-7}$ ; although the latter vibrational effects appear less important than the corresponding rotational effects for the nucleus of the same type, all these values are clearly smaller than  $Y_{0,2}^{(0)}$  by a factor comparable with the ratio  $m_e/\mu \sim 8 \ge 10^{-5}$  of electronic mass to atomic reduced mass and have much larger magnitudes than the error  $\delta Y_{0,2}^{(0)}$ . For this reason the relation  $D_e = 4B_e^3/\omega_e^2$  attributed to Kratzer is only approximate, relative to experimental error, whereas the relation  $U_{0,2} = -4U_{0,1}^3/U_{1,0}^2$ is exact and must be imposed in analyses of spectra of CO based on the reduction in Eq. (8) [28]; for other molecular species the Kratzer relation might appear to be nearly obeyed if the coefficients  $Z_{0,2}^{r,C}$  and  $Z_{0,2}^{r,O}$  had comparable magnitudes but opposite signs, or if there were an equivalent tendency of cancellation between the various combinations of  $Z_{0,2}^{v}$  and  $Z_{0,2}^r$  for the same nuclei; all these term coefficients of CO have the same sign, opposite to the sign of  $Y_{\mathfrak{R},2}^{(0)}$ .

For l = 0 and any value of k, the additional rotational effects represented by  $Z_{k,0}^r$  are identically zero. For the particular case k = 1 and l = 0, the vibrational coefficients  $Z_{0,1}^{v,C} = 7.2232$  and  $Z_{1,0}^{v,O} = -0.7212$  have values that we compare with  $Y_{1,0}^{(0)} = 216974.9287$ ,  $\delta Y_{1,0}^{(0)} = 60.0096$  and  $Y_{1,0}^{(2)} = -0.1490$ . As before, the combined adiabatic and nonadiabatic

vibrational effects have much larger magnitudes than the Dunham correction  $Y_{1,0}^{(2)}$ , which is in turn much larger than the experimental error  $\delta Y_{1,0}^{(0)}$ . In this case the contribution to the vibrational energy from the carbon nucleus in  $Z_{1,0}^{v,C}$  is much larger than that from oxygen in  $Z_{1,0}^{v,O}$ , unlike the case for which k = 0 and 1 = 1; there the corresponding values have comparable magnitudes. Whether this disparity of magnitudes for k = 1 and 1 = 0reflects the interplay between the adiabatic and the nonadiabatic vibrational effects within the composite terms [8] cannot at present be established.

## V. DISCUSSION

There have been reported two other recent fits of large collections of vibrationrotational spectral data of CO. In one case [29] the data set consisted of only 10866 lines that lacked not only the solar lines of large values of J[19] and all the vibration-rotational data of  ${}^{14}C^{16}O[20]$  that were previously published but also some recently reported precise pure rotational lines [26] of  ${}^{12}C^{16}O$ ; some of these data were however used as tests of the fitted parameters. No account of the rotational g-factor was taken in the value of  $R_e$  [29] which is hence subject to systematic error; the deviation between that value and the more fundamentally based value in Table I is however less than two standard errors. Because the generation of the effective spectral coefficients  $Y_{kl}$  or the band parameters  $G_v, B_v, D_v$ etc. is a trivial operation from the known values of the parameters in the radial functions in Table I according to the published expressions [8,12] we refrain from presenting here all these subsidiary results.

In another analysis [19] a model according to Eq. (8) was used to fit about 18500 lines that essentially constituted also the body of our data set but which we supplemented by further pure rotational lines and the lines of  ${}^{14}C{}^{16}O$ . Constraints were applied to ten values of  $U_{kl}$ ,  $k + 1 \leq 5$ , but four others were freely fitted; of the latter, the values of their expressions in terms of other parameters indicates that deviations between fitted and values calculated from  $U_{k,0}$  and  $U_{k,1}$  were 26 times the nominal standard error for  $U_{4,2}$ , 11 times for  $U_{2,4}$  (if the printed sign is not a typographical error) and six times for  $U_{0,6}$ , but only 0.3 times for  $U_{1,5}$ . Unlike the masses specified in that paper [19], our masses are taken from the latest (1985) standard compilation [30], and the values of the fundamental physical constants [31] that enter our calculations of  $R_e$  and  $k_e$  are also the latest available in a consistent set. Some parameters, for instance  $\Delta_{3,0}^O$  and  $\Delta_{0,2}^O$ , were relatively poorly determined [19]. In fits to a similar model based on Eq. (8) we found that  $U_{7,1}$  was also not significantly determined, although because of the nonlinear dependence of the coefficients  $c_j$ for potential energy the coefficients  $c_{13}$  and  $c_{15}$  have moderately significant values according to Table I which implies that significant values of  $U_{7,1}$  and  $U_{8,1}$  might be determined.

A major advantage of our analytic approach is that there prevail exact relationships

between the coefficients  $s_j, t_j$  and  $u_j$  (with their associated parameters  $c_j$  for potential energy) and the purely empirical coefficients  $\Delta_{kl}$  (for a nuclide of the same atomic number) according to Eq. (8), just like the analogous relationships [12] between the parameters  $c_j$  and the term coefficients  $Y_{kl}$  or  $U_{kl}$ . The analytic relationships between the radial coefficients  $c_j, s_j, t_j$  and  $u_j$  and the term coefficients  $Y_{kl}, Z_{kl}^r, Z_{kl}^v, U_{kl}$  and  $\Delta_{kl}$  maintain a simple form even if the actual expressions become long for large values of j. For this reason our approach is advantageous over numerical approaches such as that in Ref. [29], apart from the fact that according to no existing wholly numerical approach is there the capability to distinguish correctly in principle the various adiabatic, nonadiabatic rotational and nonadiabatic vibrational effects.

For comparison with our precise result in Table I, a few estimates of the equilibrium internuclear separation  $R_e$  of CO after all mass effects are eliminated have appeared over the years, but most values are irrelevant now because of greatly improved accuracy and extended range of spectral measurements. A value (1.1282427  $\pm$  0.0000007) x10<sup>-10</sup> m by Watson [32] took account of neither the rotational g factor nor the errors in the physical constants, whereas Bunker's value [33] (1.12823  $\pm$  0.00005) x 10<sup>-10</sup> m from older spectral data agrees well with our value within his stated error. Even when improved values of parameters of CO were derived from more modern spectra, there has in some cases been little interest in this molecular property, and almost never any explicit calculation of the molecular property  $k_e$ . Coxon and Hajigeorgiou generated a value  $R_e = (1.12822779 \pm 0.00000097) \times 10^{-10}$ m by taking account of neither the rotational g factor (which was entirely ignored in their analysis) nor the uncertainty of the physical constants [29]. Our uncertainty has the same magnitude as theirs, despite our inclusion of this necessary contribution to the total uncertainty. Their value thus deviates from our value, which is more accurate because we considered explicitly this g value, but only slightly, specifically by 1.5 standard errors, because  $g_J$  of CO has a relatively small magnitude [21].

# **VI. CONCLUSION**

According to this method of inversion of vibration-rotational spectral data [34], reduction is made directly to the coefficients of the applicable radial functions that are independent of nuclear mass. By this means we have generated the functions for potential energy, adiabatic effects and nonadiabatic rotational effects to the extent that these effects are experimentally separable; otherwise combinations of adiabatic and nonadiabatic vibrational effects, and of nonadiabatic rotational and vibrational effects, are evaluated for the diatomic molecular species CO in its ground electronic state X  ${}^{1}\Sigma^{+}$ . The value of the equilibrium internuclear distance  $R_{e}$  in the table is the most accurate available for comparison with results of ab initio calculations. By means of only 27 independent parameters of these radial sults of ab initio calculations. By means of only 27 independent parameters of these radial functions, we have reproduced the frequencies and wavenumbers of about 12300 distinct transitions of isotopic variants containing combinations of  $^{12,13,14}$ C and  $^{16,17,18}$ O within approximately the experimental uncertainties of their measurement. Of these 27 parameters, 19 have a well defined attribution (namely to potential energy, to adiabatic effects and to nonadiabatic rotational effects); the remaining eight parameters have hybrid character (either mixed adiabatic and nonadiabatic vibrational or mixed nonadiabatic rotational and vibrational) because of insufficient experimental data to allow at present their complete resolution.

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\*Electronic mail to JFO at cc7b0001@twnmoe10.bitnet

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