May, 1984] © 1984 The Chemical Society of Japan **NOTES** Bull. Chem. Soc. Jpn. 57, 1407—1408 (1984) 1407

Vibrational Energy Levels and Infrared Absorption Intensities of Carbon Monoxide

Tomoo Miyazaki,* Azuma Matsuura, and Hisao Takeuchi
Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University, Ohkubo, Shinjuku-ku, Tokyo 160

(Received July 14, 1983)

Synopsis. The vibrational energy levels and infrared absorption intensities of carbon monoxide have been calculated with due consideration for the mechanical and electrical anharmonicities of vibration by the use of ab initio molecular orbital calculation in which the C-I treatment and polarization functions were introduced.

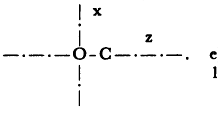
The dipole moment of carbon monoxide, as a function of the interatomic distance, is a problem of absorbing interest not only in itself but in relation to the infrared absorption intensity. In this paper, the potential energy of the CO vibration and the dipole moment function have been studied by comparison between theoretical values and observations about the wave number and intensity in the infrared absorption spectrum of carbon monoxide. One of the remarkable features of this work is that the infrared absorption intensities are calculated by the use of a dipole moment function involving the higher order terms and by vibrational wave functions obtained from the variation method in which the potential energy function involving the higher order terms are adopted. Another feature is that the atomic polarizations of the C and O atoms which bring about the unexpected dipole moment of the CO molecule are determined. The calculations have been performed by employing the GAUSSIAN 76 and 80 programs provided by the QCPE and HITAC M-280H/M-200H system of the Computer Center in The University of Tokyo.

In the first step of this work, the results of several ab initio calculations on the dipole moment (μ), gross atomic population (P_{AA}), force constant (K), and total energy (E) at the theoretical equilibrium distance (R_{eq}) of the CO molecule were compared with observations. These values are listed in Table 1. Generally, the application of CI treatment leads to a slight increase of the theoretical bond distance and to a slight decrease of the theoretical force constant. On the basis of these results, we chose the STO-6G-CI and 6311G*-CI meth-

TABLE 1. COMPARISON OF RESULTS FROM SEVERAL AB INITIO CALCULATIONS OF CO

Method[a,b,c]	R_{eq}/Å	μ[d)]/D[e)]	P_{oo}	P_{cc}	K/mdyn Å^{-1} [e)]	E/a.u.[e)]
STO-6G	1.1458	−0.0578	8.2148	5.7852	24.283	−112.30421
STO-6G-CI	1.1802	−0.2442	8.1614	5.8386	19.580	−112.43701
631G	1.1307	+0.5728	8.3492	5.6508	21.078	−112.66722
631G-CI	1.1942	+0.5402	8.3536	5.6464	21.044	−112.77613
631G*	1.1136	+0.2625	8.2777	5.7223	24.231	−112.73734
631G*-CI	1.1396	+0.1648	8.2620	5.7380	20.231	−112.85647
6311G	1.1237	+0.4677	8.3276	5.6724	20.968	−112.69949
6311G-CI	1.1439	+0.4909	8.3237	5.6763	18.265	−112.90340
6311G*	1.1047	+0.1532	8.1863	5.8137	24.076	−112.76948
6311G*-CI	1.1216	+0.1679	8.1801	5.8199	21.558	−113.05573
Obsd	1.1283	−0.112			19.02	−113.377

a) The Gaussian 76 was employed on all cases except for 6311G and 6311G* methods with or without CI treatment. b) The CI calculation for the STO-6G method was performed by considering all possible singly and doubly excited configurations. The CI calculations were performed by considering single and double excitations within the limits of orbital number 3 to 14 and 3 to 15 for the 631G and 631G* methods respectively. c) The CI calculation with Gaussian 80 was performed by considering all double excitations under condition of a frozen core. d) The Cartesian axis used in this calculation is as follows:



e) 1 D = 10^{-18} g$^{1/2}$ cm$^{5/2}$ s^{-1}, 1 mdyn Å^{-1} = 10^5 g s^{-2}, 1 a.u. = 4.35981×10^{-11} g cm^2 s^{-2}.

TABLE 2. COEFFICIENTS OF POTENTIAL ENERGY, V, AND DIPOLE MOMENT, μ, FUNCTIONS

$$V(Q)^{a)} = (1/2)\lambda Q^2 + gQ^3 + hQ^4 + iQ^5 + jQ^6$$

$$\mu(Q)^{a)} = \mu_o + M_1Q + M_2Q^2 + M_3Q^3 + M_4Q^4$$

	Coefficients of $V(Q)$			Coefficients of $\mu(Q)$[d)]	
	STO-6G-CI[b)]	6311G*-CI[c)]		STO-6G-CI[b)]	6311G*-CI[c)]
λ	0.82872×10^{29}	0.82784×10^{29}	μ_0	-0.2442×10^{-18}	0.1679×10^{-18}
g	-0.51761×10^{49}	-0.51565×10^{49}	M_1	4.90130×10	13.00971×10
h	0.21014×10^{69}	0.20980×10^{69}	M_2	0.50706×10^{21}	1.07712×10^{21}
i	-0.06554×10^{89}	-0.06898×10^{89}	M_3	-0.58929×10^{41}	-0.71974×10^{41}
j	0.01889×10^{109}	0.01920×10^{109}	M_4	-0.11907×10^{61}	-0.03150×10^{61}

Unit: Q = g$^{1/2}$ cm, V = g cm^2 s^{-2}, $\mu=\mu_0$ = g$^{1/2}$ cm$^{5/2}$s^{-1}.
a) L/g$^{-1/2}$ = 2.962707×10^{19} (The unit of internal coordinate, R, in $V(R)$ is Å.). b) $\alpha=0.989$. c) $\alpha=0.935$. d) $\mu(Q)=-0.1120\times10^{-18}+9.2130\times10Q-0.1317\times10^{21}Q^2-0.6148\times10^{41}Q^3$ (from Young and Eachus, Ref. 3), $\mu(Q)=-0.1140\times10^{-18}+9.3362\times10Q-0.2196\times10^{21}Q^2-0.6184\times10^{41}Q^3$ (from Weisbach and Chackerian, Ref. 4), $\mu(Q)=-0.2600\times10^{-18}+9.6666\times10Q-0.0031\times10^{21}Q^2-0.8924\times10^{41}Q^3$ (from Kirby-Docken and Liu, Ref. 5).

TABLE 3. ENERGY LEVELS AND WAVE FUNCTIONS OF THE CO VIBRATION[a)] (ε_v AND $\psi_v=\sum C_{vi}\phi_i^{\circ}$)

v	0	1	2	3	4	5
$\varepsilon^{b)}\times10^{13}$	2.14112	6.39337	10.60736	14.78342	18.92199	23.02403
C_{v0}	**0.99848**	−0.05312	0.00156	−0.01344	0.00559	−0.00148
C_{v1}	0.05308	**0.98686**	−0.14888	0.01308	−0.02629	0.01498
C_{v2}	0.00251	0.14861	**0.94987**	−0.26687	0.04033	−0.04163
C_{v3}	0.01454	0.01552	0.26588	**0.87239**	−0.39122	0.08764
C_{v4}	0.00169	0.03006	0.04422	0.38887	**0.74353**	−0.50298
C_{v5}	0.00012	0.00725	0.05060	0.09173	0.49871	**0.55994**
C_{v6}	0.00047	0.00110	0.01868	0.07805	0.15723	0.57409
C_{v7}	0.00008	0.00136	0.00426	0.03793	0.11397	0.23428
C_{v8}	0.00001	0.00042	0.00317	0.01160	0.06659	0.15830
C_{v9}	0.00002	0.00008	0.00134	0.00680	0.02562	0.10519
C_{v10}	0.00000	0.00008	0.00036	0.00339	0.01367	0.04853
C_{v11}	0.00000	0.00003	0.00022	0.00118	0.00739	0.02533
C_{v12}	0.00000	0.00001	0.00010	0.00060	0.00307	0.01439
C_{v13}	0.00000	0.00000	0.00003	0.00028	0.00130	0.00591

a) The values were obtained from the 6311G*-CI method. b) ε = g cm^2 s^{-2}.

TABLE 4. WAVENUMBERS, $\tilde{\nu}$, AND ABSORPTION INTENSITIES, $A_{v'\leftarrow v}$, OF THE VIBRATIONAL SPECTRUM OF CO ($\tilde{\nu}$ = cm^{-1}, A = cm^2 s^{-1} molecule^{-1}, T = 300 K)

v→v′	STO-6G-CI		6311G*-CI		Ref.	
	$\tilde{\nu}$	$A\times10^{10}$	$\tilde{\nu}$	$A\times10^{10}$	$\tilde{\nu}$[a)]	$A\times10^{10}$
0→1	2141.78	833.559	2140.79	5894.890	2143.27	2923.2[b)] 4043.2[c)] 7300.7[d)]
1→2	2122.46	0.057272	2121.52	0.408735	2116.79	
2→3	2103.41	0.000003	2102.42	0.000023	2090.38	
3→4	2084.72	0.000000	2083.55	0.000000	2064.03	
0→2	4264.24	2.09954	4262.31	16.63066	4260.06	21.056[b)] 26.210[c)]
1→3	4225.87	0.000233	4223.95	0.001777	4207.17	
2→4	4188.13	0.000000	4185.98	0.000000	4154.41	
0→3	6367.65	0.004708	6364.73	0.018628	6350.44	0.11984[b)] 0.34720[c)]
1→4	6310.59	0.000001	6307.50	0.000003	6271.20	
2→5	6254.78	0.000000	6251.14	0.000000	6192.16	
0→4	8452.37	0·000556	8448.28	0.000113	8414.47	
1→5	8377.24	0.000000	8372.66	0.000000	8308.95	

Rotational constants (cm^{-1}): $B_e=1.9531$, $\alpha_e=1.4390\times10^{-2}$, $\gamma_e=2.760\times10^{-5}$, $\delta_e=2.027\times10^{-7}$.
a) Values calculated using vibrational constants from Mantz *et al.* (Ref. 6). b) Experimental values from Young and Eachus (Ref. 3). c) Values calculated by Billingsley and Krauss (Ref. 7). d) Value calculated by Rogers and Hillman (Ref. 8).

TABLE 5. DIPOLE MOMENTS, μ, ATOMIC POLARIZATIONS, μ_{AP}, AND GROSS ATOMIC POPULATIONS, P_{AA}, AT SEVERAL CO DISTANCES (ΔR=Å, μ=Debye (10^{-18} $g^{1/2}$ $cm^{5/2}$ s^{-1}))

ΔR	STO-6G-CI					6311G*-CI				
	μ	μ^{o}_{AP}	μ^{c}_{AP}	P_{oo}	P_{cc}	μ	μ^{o}_{AP}	μ^{c}_{AP}	P_{oo}	P_{cc}
−0.08	−0.3731	+1.5450	−2.9951	8.1828	5.8172	−0.1972	+1.3769	−3.0997	8.1377	5.8623
−0.04	−0.3100	+1.5457	−2.8714	8.1710	5.8290	−0.0176	+1.3868	−3.0054	8.1572	5.8428
R_{eq}	−0.2442	+1.5328	−2.7502	8.1614	5.8386	+0.1679	+1.3816	−2.9211	8.1801	5.8199
+0.08	−0.1079	+1.4781	−2.5135	8.1473	5.8527	+0.5508	+1.3388	−2.7614	8.2320	5.7680
+0.16	+0.0277	+1.3987	−2.2812	8.1370	5.8630	+0.9418	+1.2722	−2.6074	8.2861	5.7139

ods which differ from each other in adoption of the basis set. In the next step, the detailed calculation have been performed using these two methods. According to the method of least squares, the potential energy and dipole moment functions were obtained carefully from sufficient data for distorted molecules as the higher order equations with respect to the internal coordinate (R_{CO}). These equations have been transformed to the functions with the normal coordinate (Q) by the use of the L term which relates the internal coordinate to the normal coordinate. In order to obtain the appropriate final results, these functions have been rewritten by multiplying the coordinate term by an adjusting constant (α) determined in comparison with the observed frequency of fundamental band. Table 2 records the coefficients of these potential energy and dipole moment functions. The variation method has been used to calculate the energy levels of vibration in view of the mechanical anharmonicity and the wave function (ψ) of the molecular vibration has been described by the linear combination of harmonic oscillator wave functions(ϕ°). Further details of the treatment were reported in previous papers.[1,2] The calculated energy levles and wave functions are listed in Table 3. By the use of these anharmonic wave functions and dipole moment function indicated in Table 2, the absolute infrared absorption intensities of fundamental and overtone bands have been calculated in view of the mechanical and electrical anharmonicities.[1,2] The results are summarized in Table 4 in which reference data are also included. Since the potential energy function is modified by the use of the adjusting constant (α), the calculated wave number of the fundamental band agrees well with the observed value. The calculated wave numbers of overtone bands, too, almost coincide with the observed values. From these results, we may reasonably conclude that the potential energy function obtained in this work is adequate. Furthermore, according to the perturbation treatment,[9] the rotational constants α_e, γ_e, and δ_e have been determined by the use of anharmonic wave functions as indicated in Table 3. The calculated constants are listed in the footnote of Table 4.

When the higher approximate treatment of molecular orbital calculation was adopted, the appropriate value of the dipole moment could not always be obtained. However from Table 4, in which theoretical values of infrared absorption intensities are compared with experimental values, it has been definitely recognized that the values of M_1, M_2, and M_3 in dipole moment function are improved by employing the higher approximate 6311G* calculation than STO-6G, while Amore-Bonapasta[10] reported as follows: the agreement between experimental result and theoretical function from the STO-6G method is satisfactory and better than that between experimental and 631G functions.

The last point to which special attention should be paid is the change of the direction of the dipole moment in the vicinity of the equilibrium CO distance. The values of the atomic polarization resulting from the mixing of the S and P type orbitals or the P and D type orbitals are indicated in Table 5 in which gross atomic populations are also indicated. It is notable that the absolute value of the atomic polarization, μ^{c}_{AP}, of carbon is about double that, μ^{o}_{AP}, of oxygen. The sign of μ^{c}_{AP} is negative and that of μ^{o}_{AP} is positive when the CO molecule is fixed in the coordinate indicated in the footnote of Table 1. From these results, it is evident that the unexpected sign of the CO dipole moment is caused by atomic polarizations. In the results from different methods, there are opposite tendencies as to the increase in gross atomic population with the variation of CO distance. The same tendencies are seen in the value of the dipole moment with the exception of the atomic polarization term. In view of the above facts, it is found that the theoretical result for the electronic property of carbon monoxide is highly sensitive to the difference of approximation in the method of calculation.

References

1) T. Miyazaki and H. Yamamoto, *Bull. Chem. Soc. Jpn.*, **45**, 1669 (1972).

2) T. Miyazaki, M. Ikeda, and M. Shibata, *Bull. Chem. Soc. Jpn.*, **48**, 1138 (1975).

3) L. A. Young and W. J. Eachus, *J. Chem. Phys.*, **44**, 4195 (1966).

4) M. F. Weisbach and C. Chackerian, *J. Chem. Phys.*, **59**, 4272 (1973).

5) K. Kirby-Docken and B. Liu, *J. Chem. Phys.*, **66**, 4309 (1977).

6) A. W. Mantz, J. P. Maillard, W. B. Roh, and K. N. Rao, *J. Mol. Spectrosc.*, **57**, 155 (1975).

7) F. P. Billingsley and M. Krauss, *J. Chem. Phys.*, **60**, 4130 (1974).

8) J. D. Rogers and J. J. Hillman, *J. Chem. Phys.*, **77**, 3615 (1982).

9) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley & Sons, New York (1944), p. 269.

10) A. Amore-Bonapasta, *Indian J. Chem., Sect. A*, **21**, 91 (1982).