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Molecular Structure and the Effect of Large-Amplitude Vibration of Carbon Suboxide as Studied by Gas Electron Diffraction

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The molecular structure of carbon suboxide, C_3O_2, has been studied by the sector-microphotometer method of gas electron diffraction. The C=O and C=C distances (r_g) have been determined to be $1.163_2 \pm 0.001_3$ Å and $1.289_4 \pm 0.002_2$ Å, respectively, where the uncertainties represent estimated limits of error. The observed mean amplitudes for three nonbonded atom pairs and their shrinkages are found to be much larger than those expected for ordinary molecules with linear framework. A usual harmonic approximation up to the quadratic terms of displacements cannot account for the observed values in this molecule. This indicates that the π_u bending vibration ν_7 has a very low frequency (an *effective* frequency being about 68 cm^{-1}) and that this vibration is essentially a bending motion of the valence angle of the central carbon atom, in agreement with recent spectroscopic studies. The effect of the large-amplitude vibration on mean amplitudes and shrinkages has been studied in detail by using a model, which assumes that atomic motions take curvilinear paths in the ν_7 vibration with the valley in the potential surface running along the loci of fixed bond lengths. The potential function for this bending motion has been estimated by a least-squares analysis on the observed structural parameters. The potential function is given by $V(Q_7) = (23 \pm 5)Q_7^4 - (100 \pm 31)Q_7^2$ (cm^{-1}), where the uncertainties representing random standard errors take the upper and lower signs in the same order and $Q_7 = \sin\alpha/0.145$ ($amu^{1/2}$ Å). The potential rises steeply with increasing angle of bending, $\alpha = 1/2[180° - \angle(C=C=C)]$, and appears to have a small hump at $\alpha = 0$. This "quasi-linear" potential function is consistent with the recent experimental estimates by Seip *et al.* within experimental errors, but the double-minimum nature of the potential is subject to a further critical examination by other experimental methods.

Carbon suboxide has presented a number of problems with regard to its structure and spectra. From a naive valence consideration, this molecule should have a linear equilibrium structure. However, no definite conclusion about its structure has been drawn in spite of various spectroscopic in-

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vestigations.[1-5] The infrared and Raman spectra of this molecule were so complex that they were once regarded as evidence for a nonlinear structure.[1-3] Lafferty *et al.*[5] reported that their high-resolution vibration-rotation spectrum in the 3170 cm^{-1} region could be assigned satisfactorily as a linear symmetric structure. Their analysis also indicated that the lowest bending fundamental mode was very low, probably between 25—70 cm^{-1}. This was consistent with the entropy measurements by McDougall and Kilpatrick;[6] they estimated ν_7 to be 61.6 ± 2.6 cm^{-1} on the assumption of a rigid rotor and harmonic vibrations. The first successful detection of ν_7 was reported in 1965 by Miller *et al.*,[7] who observed a very weak and broad absorption band with a maximum around 63 ± 2 cm^{-1}.

The finding of the ν_7 band, however, by no means answered all the problems in the infrared spectrum of carbon suboxide. In order to explain a number of anomalous features in the spectra, Pitzer and Strickler[8] and later Miller *et al.*[7] suggested that this CCC bending vibration may be highly anharmonic like the low-frequency bending mode in diazomethane. On the other hand, Bell *et al.*[9] claimed that the anharmonicity constant x_{77} must be small, although the interaction with other fundamental vibrations may be large. With regard to the details of the CCC bending potential function, controversial remarks have been made. Redington[10] fitted a two-term potential function for this bending motion to the spectra observed by Miller *et al.*[4,7] using the theory of Thorson and Nakagawa[11] and suggested that the potential was relatively flat-bottomed, being characteritic of a quasi-linear molecule. Almenningen *et al.*[12] favored a potential with a barrier at a linear structure on the basis of their analysis of electron-diffraction data.

The interatomic distances in carbon suboxide were determined by the Norwegian group by electron diffraction at three different temperatures (237°K, 290°K, 508°K).[12] Their results at room temperature were $r(C=C)=1.2898\pm0.0036$ Å and $r(C=O)=1.1655\pm0.0021$ Å, which are consistent with the earlier results of Livingston and Rao,[13] and of Mackle and Sutton,[14] both by the visual method. These earlier results were used by Lafferty *et al.*[5] to prefer one of their assignments on the π-π transitions in a vibration-rotation band.

The presence of a low-frequency vibration should have a significant influence on some of the structural parameters observed by gas electron diffraction. The study of such anomalous vibrational effects by a diffraction method should supply useful information, which is hard to obtain by other methods, on the potential function. Accordingly, the present study aims to make a precise analysis of the mean amplitudes and shrinkages so as to shed light on this problem.

Experimental

The sample of carbon suboxide was prepared by the dehydration of malonic acid in vacuum[15] using glass tubes and stopcocks with KEL-F stopcock grease. Twenty grams of malonic acid, 200 g of fresh powdered phosphorus pentoxide and 40 g of roasted sand were mixed in a 1*l* flask, which was attached to a vacuum system with a sample holder and a U-tube of 20 mm diameter. Towers packed with glass-wool and with calcium oxide were inserted between the U-tube and the sample holder. The flask was heated for two hours on an oil-bath at 140 to 150°C under about 10^{-2} mmHg, and volatile products (carbon suboxide, carbon dioxide, and acetic acid) were condensed in a U-tube cooled to liquid-nitrogen temperature. The U-tube was then put in a dry ice-acetone bath, and the gaseous mixture of carbon dioxide and carbon suboxide was allowed to pass into a sample holder cooled at liquid-nitrogen temperature. Carbon dioxide was then distilled off at dry ice-acetone temperature until the vapor pressure decreased to about 6 mmHg, the pressure of carbon suboxide measured by Stock and Stolzenberg.[15] A gas-chromatographic analysis of the product showed that the sample was more than 99% pure. It was possible to store the sample at liquid-nitrogen temperature for over a month without decomposition.

Diffraction photographs were taken on Fuji Process Hard plates at 20°C with an apparatus equipped with an r^3-sector.[16] The sample stored in a 2*l* flask with a pressure of about 40 mmHg at 20°C was introduced into the diffraction chamber through a nozzle of 0.2 mm diamter. The camera lengths used were measured

1) H. D. Rix, *J. Chem. Phys.*, **22**, 429 (1954).
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3) B. P. Stoicheff, *Advan. Spectry.*, **1**, 124 (1959).
4) F. A. Miller and W. G. Fateley, *Spectrochim. Acta*, **20**, 253 (1964).
5) W. J. Lafferty, A. G. Maki and E. K. Plyler, *J. Chem. Phys.*, **40**, 224 (1964).
6) L. A. McDougall and J. E. Kilpatrick, *ibid.*, **42**, 2311 (1965).
7) F. A. Miller, D. H. Lemmon and R. E. Witkowski, *Spectrochim. Acta*, **21**, 1709 (1965).
8) K. S. Pitzer and S. J. Strickler, *J. Chem. Phys.*, **41**, 730 (1964).
9) S. Bell, T. S. Varadarajan, A. D. Walsh, P. A. Warsop, J. Lee and L. Sutcliffe, *J. Mol. Spectry.*, **21**, 42 (1966).
10) R. L. Redington, *Spectrochim. Acta*, **23A**, 1863 (1967).
11) W. R. Thorson and I. Nakagawa, *J. Chem. Phys.*, **33**, 994 (1960).
12) A. Almenningen, S. P. Arnesen, O. Bastiansen, H. M. Seip and R. Seip, *Chem. Phys. Lett.* **1**, 569 (1968).
13) R. L. Livingston and C. N. R. Rao, *J. Amer. Chem. Soc.*, **81**, 285 (1959).
14) H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 937 (1951).
15) A. Stock and H. Stolzenberg, *Ber.*, **50**, 498 (1917).
16) Y. Murata, K. Kuchitsu and M. Kimura, *Japan. J. Appl. Phys.*, **9**, 591 (1970).

to be 107.78±0.02 mm and 243.22±0.02 mm. The beam current was about 0.16 μA. The exposure times were about 1 and 3 minutes for the longer and shorter camera lengths, respectively. The accelerating voltage was stabilized within 0.1% during the experiment and was measured by the method of Rymer and Wright[17] to be about 39.4 kV. The wavelength of the electron beam was calibrated to within 0.07% with reference to the r_a(C=O) bond length of carbon dioxide, 1.1646 Å.

The photographic densities were measured using an integrating digital voltmeter along the diameter of the diffraction pattern at integral q values.[18] Several readings on both sides for 4 sec each were averaged. The optical densities were regulated below 0.6, where a linear relation for the conversion of optical density into electron intensity is applicable. The electron intensity was divided by a theoretical background function in order to make the background nearly flat. A slight uniform fogging observed in the region of larger scattering angles was ascribed to the reflection of scattered electrons by the sector race[16] and was subtracted from the observed total intensity.*2 No significant systematic deviations were observed among the intensities taken from different photographic plates nor from different camera lengths.

Analysis

The molecular intensity curve was obtained by drawing a smooth background through the intensity curve corrected for the imperfection in the sector opening and for the effect of non-nuclear scattering.[19] The background was revised with the aid of Karles' criterion of minimum ghosts in the radial distribution curve.[20] The atomic scattering factors, F, of carbon and oxygen were calculated from the Hartree-Fock potential expressed analytically by Strand and Bonham.[21] The inelastic scattering factors, S, and the phase shift, $\Delta\eta_{CO}=\eta_C-\eta_O$, were taken from the tables of Pohler and Hanson[22] and those of Ukaji and Bonham,[23] respectively.

The molecular parameters were determined by a least-squares fit of the observed molecular intensity (Fig. 1) to the following theoretical expression with a preestimated weight function:[24]

$$qM(q) = k\sum_{i\neq j} A_{ij}\mu_{ij}\cos\Delta\eta_{ij}\sin\frac{\pi}{10}q \times\left[r_{aij}-\left(\frac{\pi}{10}q\right)^2\kappa_{ij}\right]\exp\left[-\frac{1}{2}\left(\frac{\pi}{10}ql_{ij}\right)^2\right], \quad (1)$$

where the symbols have their usual significance. The parameters representing asymmetry, κ, for the bonded C=O and C=C atom pairs were fixed in the analysis to the values estimated by assuming the Morse potential functions.[25] The anharmonicity parameters, a_3, were assumed to be 2.39 $Å^{-1}$ and 2.13 $Å^{-1}$, respectively.[26] The κ parameters for all the nonbonded pairs were ignored. Despite the presence of a low-frequency bending vibration, the present assumption for the O_1–C_4

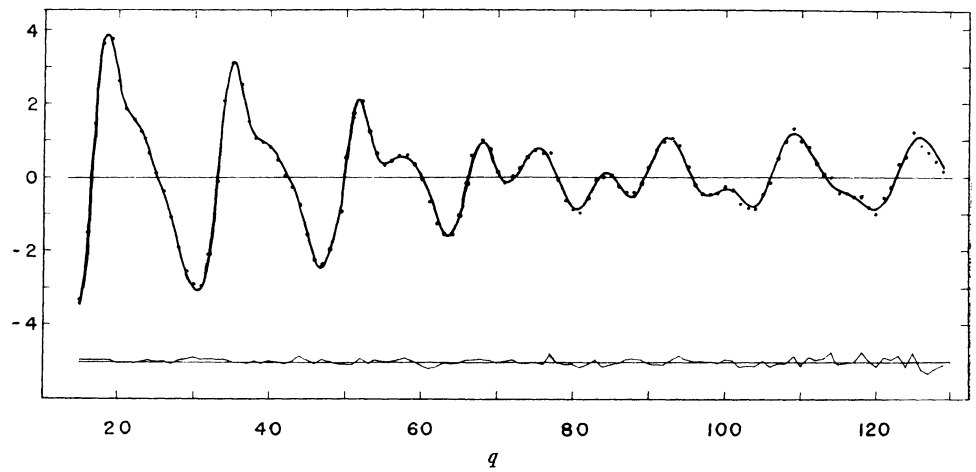

Fig. 1. Reduced molecular intensity curves (dots for observed values and the solid curve calculated from the best-fit model). The residual is shown below.

17) T. E. Rymer and K. H. R. Wright, *Proc. Roy. Soc.* (London), **A215**, 550 (1952).

18) Y. Morino, K. Kuchitsu and T. Fukuyama, This Bulletin, **40**, 423 (1967).

*2 The correction for this fogging made the calculated and observed mean amplitude for carbon dioxide and other molecules agree within the experimental error of 0.002 Å.

19) L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

20) J. Karle and I. L. Karle, *ibid.*, **18**, 957 (1950).

21) T. G. Strand and R. A. Bonham, *ibid.*, **40**, 1686 (1964).

22) R. F. Pohler and H. P. Hanson, *ibid.*, **42**, 2347 (1965).

23) R. A. Bonham and T. Ukaji, *ibid.*, **36**, 72 (1962).

24) Y. Morino, K. Kuchitsu and Y. Murata, *Acta Crystallogr.*, **18**, 549 (1965).

25) K. Kuchitsu, This Bulletin, **40**, 498 (1967).

26) K. Kuchitsu and Y. Morino, *ibid.*, **38**, 805 (1965).

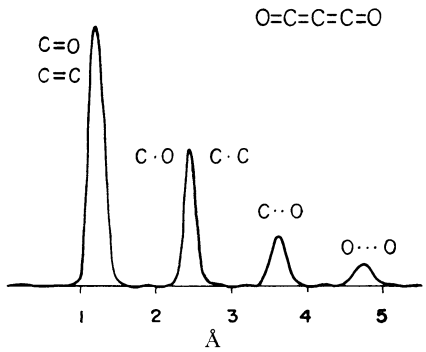

Fig. 2. Radial distribution curve calculated with an artificial damping factor, $\exp(-0.00138s^2)$.

and O_1–O_5 pairs is justified by the approximate symmetry of their radial distribution peaks (Fig. 2), which are found to fit to Gaussian functions within experimental error. It is hard to make analogous tests for the C_2–C_4 and C_3–O_1 distributions, since they overlap each other. Nevertheless, their κ parameters are possibly within the range of $\pm 10^{-6}$ Å^3,[25] and hence, the systematic errors in their distances and shrinkages due to the neglect of their κ are certainly within their quoted uncertainties.

Six atomic distances r_a, six mean amplitudes l, and the index of resolution k were determined in the analysis as variable parameters. The most probable values of the parameters with their limits of error are given in Tables 1 and 2.*3 The mean value of an internuclear distance averaged over the probability distribution function, $\langle r \rangle$ or r_g, is related to r_a as[25] $r_g = r_a + l^2/r_a$. The shrinkages, δ_g,[27] for nonbonded atom pairs are given in Table 3. The observed mean amplitudes and the shrinkages for the C_2–C_4, O_1–C_4, and O_1–O_5 atom pairs are much larger than for the other atom pairs, as expected from the low frequency of the ν_7 vibration. This effect is discussed in detail in the following section.

Table 1. Observed values of bond lengths in carbon suboxide at room temperature (in Å units)

	r_a	r_g	ε[a]
$O_1=C_2$	1.162_0	1.163_2	0.001_3
$C_2=C_3$	1.288_1	1.289_4	0.002_2
$O_1—C_3$	2.444_1	2.444_8	0.005_0
$C_2—C_4$	2.48_2	2.48_5	0.01_7
$O_1—C_4$	3.629_0	3.630_8	0.004_9
$O_1—O_5$	4.75_3	4.75_5	0.01_3

a) Estimated limits of error.

*3 Numerical experimental data of the leveled total intensity and their error matrix have been deposited with the Chemical Society of Japan (Document No. 7005). A copy may be secured by citing the document number and by remitting, in advance, ¥200 for photoprints. Payment by check or money order payable to: Chemical Society of Japan.

27) Y. Morino, J. Nakamura and P. W. Moore, *J. Chem. Phys.*, **36**, 1050 (1962).

Table 2. Observed and calculated values of mean amplitudes for carbon suboxide at room temperature (in Å units)

	$l_{obs.}$	$l_{calc.}$ (a)	$l_{calc.}$ (b)
$O_1=C_2$	$0.036_8 \pm 0.001_3$	0.034_9	0.034_9
$C_2=C_3$	$0.041_2 \pm 0.002_2$	0.038_5	0.038_5
$O_1—C_3$	$0.042_1 \pm 0.002_1$	0.042_0	0.043_4
$C_2—C_4$	$0.07_6 \pm 0.01_9$	0.042_4	0.071_3
$O_1—C_4$	$0.080_9 \pm 0.007_1$	0.045_1	0.084_4
$O_1—O_5$	$0.09_9 \pm 0.01_0$	0.047_3	0.095_3

(a) Harmonic approximation with ω_7 assumed to be 63 cm^{-1}.
(b) Large-amplitude analysis for ν_7 (see text).

Table 3. Observed and calculated values of shrinkages for carbon suboxide at room temperature (in Å units)

	δ_g obs.	δ_g calc. (a)	δ_g calc. (b)
$O_1—C_3$	$0.007_8 \pm 0.005_5$	0.007_1	0.007_0
$C_2—C_4$	$0.09_4 \pm 0.01_7$	0.072_3	0.087_8
$O_1—C_4$	$0.111_1 \pm 0.005_9$	0.105_2	0.111_2
$O_1—O_5$	$0.15_0 \pm 0.01_4$	0.162_7	0.151_0

(a) Harmonic approximation with ω_7 assumed to be 63 cm^{-1}.
(b) Large-amplitude analysis for ν_7 (see text).

Vibrational Effects

Conventional Calculations. *Mean Amplitudes.* If a linear equilibrium structure and small amplitudes of bending vibrations are presupposed for this molecule, the mean-square amplitudes for bonded and nonbonded atom pairs are related in the first approximation to the stretching vibrations only, namely Q_1 through Q_4. Provided the force constants representing the interactions between non-adjacent bonds are ignored and the normal frequencies are approximated by the fundamental frequencies, the force constants for the stretching vibrations can be determined uniquely, and the mean amplitudes can be calculated by a conventional method.[28] Table 2 lists the values derived in this way; they agree with those calculated by Brunvoll *et al.*[29] In striking contrast to the ex-

28) Y. Morino, K. Kuchitsu and T. Shimanouchi, *ibid.*, **20**, 726 (1952).

29) J. Brunvoll, S. J. Cyvin, I. Elvebredd and G. Hagen, *Chem. Phys. Lett.*, **1**, 566 (1968).

perience for ordinary molecules, where the present approximation is known to be valid,[30] the calculated values for the atom pairs C_2–C_4, O_1–C_4, and O_1–O_5 cannot account for the observed values. This implies that a higher-order effect due to the bending vibrations is important for the above-mentioned atom pairs.

Shrinkage Effects. The linear shrinkage effect is given by:[27]

$$\delta_g = \boldsymbol{D}[r_g], \tag{2}$$

where $\boldsymbol{D}$ stands for the operation of taking a difference of the quantity in brackets for a nonbonded atom pair and a sum of those for the component bonded pairs. If one assumes that the vibrations are *harmonic*, then the shrinkage may be approximated by the following expression:[27]

$$\delta_g = \boldsymbol{D}[(1/2r_e)\langle\Delta\rho^2\rangle], \tag{3}$$

where r_e is the corresponding bonded or nonbonded equilibrium distances and $\Delta\rho^2=\Delta x^2+\Delta y^2$ is linearly related to the squares of bending coordinates, Q_5^2, Q_6^2 and Q_7^2. The perpendicular amplitudes $\Delta\rho^2$ were calculated by the usual *GF* method,[31] with the quadratic force constant for the CCO bending transferred from the out-of-plane CCO bending constant of ketene.[32] Since the calculated shrinkages are insensitive to the differences of several wave numbers in ν_5 and ν_6, the observed fundamental frequencies ν_5 and ν_6 were used in place of the normal frequencies ω_5 and ω_6, respectively. On the other hand, the position of the maximum absorption (63 cm^{-1})[7] was tentatively substituted for the effective ω_7 frequency in order to estimate the shrinkages. Table 3 shows that the above harmonic approximation roughly accounts for the observed shrinkages.

The above conventional procedure thus fails to predict the observed mean amplitudes, although the agreement is fair for the shrinkages. The principal origin of the discrepancies in the mean amplitudes lies in the ν_7 bending vibration; the instantaneous displacements of certain nonbonded distances caused by this vibration should be much larger than those caused by the parallel vibrations ν_1 through ν_4 as a result of the large amplitude of the ν_7 vibration.

If the average values of the mass-adjusted bending coordinate ($\langle Q_7^2\rangle$ and $\langle Q_7^4\rangle$) and the ratio of the perpendicular amplitudes, $\Delta\rho_{CC}/\Delta\rho_{CO}$, are taken as parameters, one can analyze the observed mean amplitudes and shrinkages without assuming any explicit form of the potential function for the ν_7 vibration. According to a preliminary analysis of this kind,[33] the average value $\langle Q_7^2\rangle$ turns out to be about 3.0 amu Å^2, which corresponds to an effective normal frequency of *ca.* 68 cm^{-1}, being compatible with the thermodynamic and infrared results. Furthermore, the ratio $\langle Q_7^4\rangle/\langle Q_7^2\rangle^2$, which should be equal to 2 if the potential were harmonic,[*4] is estimated to be about 1.36. Thus the problem is to find a potential function that satisfies the above average values.

Large-amplitude Analysis for the ν_7 Vibration. *Hamiltonian Operator.* For ordinary triatomic molecules the potential function is expanded in terms of the normal coordinates, and the average values of interatomic displacements are calculated by a perturbation method.[34,35] However, this method is not suitable for the present problem because the large vibrational amplitude deteriorates the convergence. Thus it is simpler to use a curvilinear coordinates for this vibration at the expense of a more complicated expression for the kinetic energy. The mean amplitudes and shrinkages were calculated by the following model: The ν_7 mode is regarded as a set of doubly-degenerate slowly-varying coordinates, since this vibration has much lower frequency than the other vibrations. The atoms take curvilinear paths holding the bond distances (averaged over the vibrations ν_1 through ν_6) constant. This is equivalent to assuming that the effective force field characterizing the small-amplitude vibrations (ν_1 through ν_6) is independent of the ν_7 displacement.

Being analogous to the case of puckering motions in ring compounds[36] and that of quasi-linear molecules,[11] the reduced mass for this vibration depends on the ν_7 displacement coordinate. This was taken into account when the kinetic energy was set up in classical dynamics and converted into an operator representing the quantum-mechanical kinetic energy.

After the separation of translational motions, the ν_7 motion is described by a molecule-fixed coordinate system xyz, where the z axis corresponds to the equilibrium molecular axis, and the bending motion takes place in the xz plane, because the coupling between the ν_7 vibration and other bending modes has been ignored.

According to the above assumptions the in-

30) Y. Morino and T. Iijima, This Bulletin, **35**, 1661 (1962).

31) Y. Morino and E. Hirota, *J. Chem. Phys.*, **23**, 737 (1955).

32) G. B. Moore and G. C. Pimentel, *ibid.*, **38**, 2816 (1963).

33) M. Tanimoto, Thesis, The University of Tokyo (1969).

*4 For a doubly-degenerate harmonic oscillator, $Q_7^2=Q_{7a}^2+Q_{7b}^2$, it follows that $\langle Q_7^4\rangle=2\langle Q_7^2\rangle^2$.

34) L. S. Bartell, *J. Chem. Phys.*, **38**, 1827 (1963). A. Reitan, Thesis, Trondheim (1958).

35) Y. Morino and T. Iijima, This Bulletin, **36**, 412 (1963).

36) D. O. Harris, H. W. Harrington, A. C. Luntz and W. D. Gwinn, *J. Chem. Phys.*, **44**, 3467 (1966).

stantaneous coordinates of the atoms, $x(=\rho)$ and z, are given to a good approximation in terms of a mass-adjusted bending coordinate Q_7.

$$\left.\begin{array}{ll} O_1\ (d_1Q_7,\ -D_{12}-D_{23}) & C_2\ (d_2Q_7,\ -D_{23}) \\ C_3\ (d_3Q_7,\ 0) & C_4\ (d_2Q_7,\ D_{23}) \\ O_5\ (d_1Q_7,\ D_{12}+D_{23}) & \end{array}\right\} \quad (4)$$

where the constants d_i are equal to the $(i, 7)$ elements of the L_x matrix, usually defined for infinitesimal displacements around the linear position, and D_{ij} is defined as

$$D_{ij} = [r_{ij}^2 - (d_i - d_j)^2Q_7^2]^{1/2}. \quad (5)$$

The constants r_{12} and r_{23} represent the C=O and C=C distances, respectively, averaged over the normal modes ν_1–ν_6. Equation (4) shows that the ratio of the relative displacements of the C=C and C=O bonds in the direction of the ρ axis, $\Delta\rho_{CC}/\Delta\rho_{CO}$, assumes a constant value for the ν_7 vibration.

The kinetic energy for this motion is given by

$$2T = \sum m_i\boldsymbol{v}_i^2 + \sum m_i(\omega\times\boldsymbol{r}_i)^2 + 2\omega\cdot\sum m_i(\boldsymbol{r}_i\times\boldsymbol{v}_i), \quad (6)$$

where $\boldsymbol{v}_i$ and ω are the velocity of the atom i and the angular momentum of the molecule-fixed frame, respectively. Substitution of the coordinates $\boldsymbol{r}_i$ in Eq. (4) and their derivatives into (6) leads to

$$2T = M_7\dot{Q}_7^2 + I_{xx}\omega_x^2 + I_{yy}\omega_y^2 + I_{zz}\omega_z^2, \quad (7)$$

where M_7 is the reduced mass for the ν_7 vibration and I_{xx}, I_{yy} and I_{zz} are instantaneous moments of inertia. They are expressed in terms of Q_7 in the following way

$$\left.\begin{array}{l} M_7 = 1 + [2m_O\{(d_1 - d_2)^2/D_{12} \\ \quad + (d_2 - d_3)^2/D_{23}\}^2 + 2m_C(d_2 - d_3)^4/D_{23}^2]Q_7^2 \\ I_{xx} = 2[m_O(D_{12} + D_{23})^2 + m_CD_{23}^2] \\ I_{yy} = 2[m_O(D_{12} + D_{23})^2 + m_CD_{23}^2] + Q_7^2 \end{array}\right\} \quad (8)$$

and

$$I_{zz} = Q_7^2.$$

In terms of the momenta P_m the kinetic energy takes the following form,

$$2T = \sum G^{mn}P_mP_n \qquad (P_m = P_x, P_y, P_z, P_7) \quad (9)$$

The coefficient G^{mn} is given by a diagonal matrix with elements I_{xx}^{-1}, I_{yy}^{-1}, I_{zz}^{-1} and M_7^{-1}.

The corresponding quantum-mechanical operator is given by the relation[37]

$$2T'_{QM} = G^{1/2}\sum P_mG^{mn}G^{-1/2}P_n, \quad (10)$$

where G is the determinant of G^{mn} and the wavefunction is normalized in the Cartesian coordinate system as in the case of a degenerate bending motion in a linear triatomic molecule.[38] Since the reduced mass depends on Q_7, the density factor defined in Ref. 37 contains contributions from higher powers of Q_7, whereas the resulting differential equation is equal to that for a two-fold degenerate vibration[39] as far as the zeroth-order terms are concerned.

In order to make the density factor proportional to Q_7, the following substitution is made

$$G^{-1/2} = I_0Q_7g^{-1/2}, \quad (11)$$

where I_0 is the moment of inertia about the x-axis in the equilibrium structure and

$$g^{-1/2} = 1 + FQ_7^2 \quad (12)$$

where the coefficient F is a function of the constants A, B, and C given in Appendix 1. When the factor $g^{-1/2}$ is taken into the kinetic energy operator, the resulting operator is given by

$$\left.\begin{array}{l} T_{QM} = g^{-1/4}T'_{QM}g^{1/4} \\ \quad = \dfrac{1}{2}g^{-1/4}G^{1/2}\sum P_mG^{mn}G^{-1/2}P_ng^{1/4} \\ \quad = T_{rot} + T_{vib}, \end{array}\right\} \quad (13)$$

where the rotational energy is

$$2T_{rot} = P_x^2/I_{xx} + P_y^2/I_{yy}. \quad (14)$$

The vibrational part

$$2T_{vib} = P_7^2 - \frac{i\hbar P_7}{Q_7} + \frac{P_z^2}{I_{zz}} + 6i\hbar AQ_7P_7 - 2AQ_7^2P_7^2 - F(8A - 3F)\hbar^2Q_7^2 + F^2(2A + F)\hbar^2Q_7^4 \quad (15)$$

can be expanded in terms of a dimensionless coordinate $q_7=(2\pi c\nu/\hbar)^{1/2}Q_7$, where a constant ν, which has a dimension of frequency, can be chosen arbitrarily since it does not appear in the result of the analysis. Thus $2T_{vib}$ is divided into two parts,

$$2T_{vib} = 2T^0_{vib} + 2T'_{vib}, \quad (16)$$

where

$$2T^0_{vib} = -hc\nu\left[\frac{\partial^2}{\partial q_7^2} + \frac{1}{q_7}\frac{\partial}{\partial q_7} + \frac{1}{q_7^2}\frac{\partial^2}{\partial\chi^2}\right]$$

and

$$2T'_{vib} = 6\hbar^2Aq_7\frac{\partial}{\partial q_7} + 2\hbar^2Aq_7^2\frac{\partial^2}{\partial q_7^2} - F(8A - 3F)\hbar^3q_7^2/2\pi c\nu + F^2(2A + F)\hbar^4q_7^4/(2\pi c\nu)^2$$

The operator T^0_{vib} leads to a differential equation for a two-fold degenerate vibration, where χ represents the angular coordinate. Following the treatment of puckering motions in a number of ring compounds,[40] the potential function is assumed to have the following form

$$V(Q_7) = aQ_7^4 + bQ_7^2 \quad (17)$$

37) E. C. Kemble, "The Fundamental Principles of Quantum Mechanics," McGraw-Hill, New York (1937), Sec. 35b.

38) D. M. Dennison, *Rev. Mod. Phys.*, **3**, 280 (1931).

39) W. H. Shaffer, *ibid.*, **16**, 245 (1944).

40) S. I. Chan, T. R. Borgers, J. W. Russell, H. L. Strauss and W. D. Gwinn, *J. Chem. Phys.*, **44**, 1103 (1966); J. Laane and R. C. Lord, *ibid.*, **47**, 4941 (1967).

Thermal Average Values of Normal Coordinates. With the approximate Hamiltonian operator obtained above, the thermal average values of even powers of the normal coordinate q_7 can be calculated in a straightforward way. The Hamiltonian matrix is set up with the orthonormal set of functions which diagonalize the Hamiltonian for the two-dimensional harmonic oscillator, and the matrix is diagonalized by Jacobi's method.*5 The anharmonic mean values of q_7 are calculated by a weighted sum,

$$\langle {q_7}^{2m} \rangle = \sum_{n,l} \langle n, l | {q_7}^{2m} | n, l \rangle \times \exp(-E_{n,l}/\boldsymbol{k}T) / \sum_{n,l} \exp(-E_{n,l}/\boldsymbol{k}T) \quad (18)$$

where $\langle n,l | {q_7}^{2m} | n,l \rangle$ denotes the expectation values for a transformed function numbered with n and l.

The harmonic mean values for q_1 through q_6 are calculated by[28]

$$\left.\begin{aligned} \langle {q_i}^{2m} \rangle &= \frac{(2m)!}{4m!}\left(\coth\frac{\boldsymbol{hc}\omega_i}{2\boldsymbol{k}T}\right)^m \quad (i = 1-4) \\ \text{and} \\ \langle {q_i}^{2m} \rangle &= m!\left(\coth\frac{\boldsymbol{hc}\omega_i}{2\boldsymbol{k}T}\right)^m \quad (i = 5, 6) \end{aligned}\right\} \quad (19)$$

Mean Amplitudes and Shrinkage Effects. An instantaneous distance of an atom pair is expressed in terms of its Cartesian displacements up to the sixth power as

$$r = r_e + \Delta z + \frac{\Delta\rho^2}{2r_e} - \frac{\Delta z\Delta\rho^2}{2{r_e}^2} + \frac{\Delta z^2\Delta\rho^2}{2{r_e}^3} - \frac{\Delta\rho^4}{8{r_e}^3} - \frac{\Delta\rho^2\Delta z^3}{2{r_e}^4} + \frac{3\Delta z\Delta\rho^4}{8{r_e}^4} - \frac{\Delta\rho^6}{16{r_e}^5} - \frac{3\Delta\rho^4\Delta z^2}{4{r_e}^5} + \frac{\Delta\rho^2\Delta z^4}{2{r_e}^5} \quad (20)$$

The parallel displacement, Δz, may essentially be divided into two parts, $\Delta z_{\mathrm{I}} + \Delta z_{\mathrm{II}}$, where the first and second terms represent the changes in the projected bond length due to stretching and bending vibrations, respectively.[26] The Δz_{I} term may be expanded in terms of q_1 through q_4, while the Δz_{II} term may be expanded in terms of the perpendicular amplitudes $\Delta\rho$; by assumption the average values of the bond lengths are unchanged in the bending vibrations, so that the constraint, $\langle r \rangle = r_g$, exists for the bending vibrations. It therefore follows that

$$\Delta z_{\mathrm{II}} = ({r_g}^2 - \Delta\rho^2)^{1/2} - r_g = -\frac{\Delta\rho^2}{2r_g} - \frac{\Delta\rho^4}{8{r_g}^3} - \frac{\Delta\rho^6}{16{r_g}^5} + \cdots \quad (21)$$

for bonded atom pairs, and

$$\Delta z_{\mathrm{II}}(ij) = \Delta z_{\mathrm{II}}(ik) + \Delta z_{\mathrm{II}}(kl) + \cdots + \Delta z_{\mathrm{II}}(nj) \quad (22)$$

for nonbonded atom pairs i-k-l-$\cdots$-j. Thus, it is possible to express an instantaneous distance in terms of q_1 through q_7, and its thermal average value can be calculated by Eqs. (18) and (19).

The mean amplitudes ${l_g}^2$ may be calculated by the relation:[25]

$${l_g}^2 = \langle r^2 \rangle - \langle r \rangle^2 \quad (23)$$

and the shrinkages, δ_g, are calculated by the use of Eqs. (2) and (20).

Least-squares Analysis on Mean Amplitudes and Shrinkages. Two parameters a and b in the potential function, Eq. (17), and the ratio $\Delta\rho_{\mathrm{CC}}/\Delta\rho_{\mathrm{CO}}$, by which the shape of the ν_7 mode is specified, were used to adjust the calculated values of mean amplitudes and shrinkages. A least-squares method was applied with statistical weights estimated from the errors of their observed values. The HITAC 5020E in the Computer Centre of the University of Tokyo was used for this analysis. Thermal averages of the q_7 coordinate were calculated by solving a matrix of 30×30. The parameters a, b, and $\Delta\rho_{\mathrm{CC}}/\Delta\rho_{\mathrm{CO}}$ were refined until the deviations of the calculated values for the mean amplitudes and shrinkages were in the limits of their experimental errors. The final values of the determined parameters are listed in Table 4 with their estimated standard errors[41] and the parameters representing the vibrational coordinate.*6 The mean amplitudes and shrinkages calculated from the parameters are listed in the last columns of Tables 2 and 3, respectively. The $\Delta\rho$ ratio is estimated to be 1.30 ± 0.10. If the C=O and C=C bonds stay colinear in the ν_7 mode, the ratio should be equal to $r_{23}/r_{12}=1.10$. Thus the CCO angle does not deviate far from 180° in the ν_7 mode. The half bending angle,[19] $\alpha = 1/2[180° - \angle(\mathrm{C{=}C{=}C})]$, is related to Q_7 as $\sin\alpha = \Delta\rho_{\mathrm{CC}}/r_{\mathrm{CC}} = 0.145\ Q_7$.

*5 Perturbing terms involved in T'_{vib} do not mix states with different values of l, and hence, a separate matrix can be set up for each l value. Since v and l have the same parity, the rows and columns of a matrix for a given l are labeled by a series of either even or odd v numbers according to whether the l is even or odd.

41) Y. Morino and T. Nakagawa, *J. Mol. Spectry.*, **26**, 496 (1968).

*6 In our preliminary analysis, where the perturbing terms in the kinetic energy operator, T'_{vib}, were ignored and a first-order perturbation method was used, the potential function was estimated to be $V = 1.35{Q_7}^4 + 43.6{Q_7}^2$ (cm^{-1}). This potential function was cited by Pickett and Strauss[42] in their calculation of the statistical entropy (61.94 cal/deg·mol). However, a subsequent, more rigorous procedure described in this article has shown that the first-order treatment is not accurate enough and the T'_{vib} terms make a significant contribution to $\langle {Q_7}^2 \rangle$ and $\langle {Q_7}^4 \rangle$. The values listed in Table 4 replace the above estimates. The presented study still ignores stretching-bending interactions, by which the C=O and C=C stretching force constants may change slightly with angle deformation.

42) H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, **51**, 952 (1969); H. L. Strauss, private communication (1970).

TABLE 4. POTENTIAL CONSTANTS AND DYNAMICAL PARAMETERS CHARACTERIZING THE ν_7 BENDING MODE[a]

a	b	$\Delta\rho_{CO}/\Delta\rho_{CO}$	V_0[c]
23 ± 5[b] $cm^{-1}\,amu^{-2}Å^{-4}$	-100 ± 31[b] $cm^{-1}\,amu^{-1}Å^{-2}$	1.30 ± 0.10	110 ± 47[d] cm^{-1}

$\langle Q_7^2\rangle$	$\langle Q_7^4\rangle$	d_1	d_2	d_3
2.98 ± 0.10[d] $amuÅ^2$	$12.0_9\pm0.7_7$[d] $amu^2Å^4$	-0.110[e] $amu^{-1/2}$	0.035[e] $amu^{-1/2}$	0.222[e] $amu^{-1/2}$

a) Derived from a least-squares analysis on the observed mean amplitudes and shrinkages. The potential function is expressed as: $V(Q_7)=aQ_7^4+bQ_7^2\,cm^{-1}$, where $\sin\alpha=0.145Q_7$.
b) Random standard errors. The upper and lower signs should be taken in the same order because of the correlation of the parameters a and b.
c) Potential hump. See Fig. 3.
d) Evaluated from the standard deviations with allowance for the correlation among the parameters (Ref. 41). The uncertainties represent standard deviations. No systematic error due to the assumption made in the analysis is included.
e) Coefficients of the atomic ρ coordinates. Eq. (4).

Discussion

Bond Length. The r_a distances for the C=O and C=C atom pairs agree with the distances reported in earlier investigations within their limits of error.[12-14] The C=O bond length (r_g=(C=O)=1.163_2 Å) is shorter than that in carbon dioxide ($r_g=1.165_1$ Å) and is nearly the same as that in ketene ($r=1.16_1$ Å).[43] The distance between adjacent carbon atoms linked with a double bond, $r_g(C=C)=1.289_4$ Å, is appreciably shorter than 1.311_6 Å in allene[44] and nearly equal to 1.283 Å of the central C=C bond in butatriene.[45] A general rule, suggested by Stoicheff *et al.*[46] for the estimation of CC bond lengths from the number of adjacent atoms, leads to 1.282 Å in this case, in good agreement with the experimental r_g value.

Potential Function. The potential function for the bending mode ν_7, calculated with the values of a and b obtained above, is illustrated in Fig. 3. The potential energy rises steeply with increasing angle of bending, and possibly a small potential hump of the order of 100 cm^{-1} exists at the linear position. The potential nimimum appears at the α angle of about 12°. The random standard errors in the parameters listed in Table 4, not including systematic errors originating from the assumptions on which the present analysis is based, result in the uncertainties indicated as vertical bars in the figure. There is little doubt as to the quasi-linearity of the potential function for the ν_7 mode in spite of the above assumptions, whereas the double-minimum nature of the function, which is obscured appreciably by random and systematic uncertainties, is subject to a further critical examination by other experimental methods.

This potential function is consistent with those reported by Almenningen *et al.*,[12] who first suggested a double-minimum potential with humps ranging from 40 to 255 cm^{-1}. The mean amplitudes and shrinkages for 237°K and 508°K, calculated from the potential function given in Table 4, are found to be consistent with their observed values within their experimental uncer-

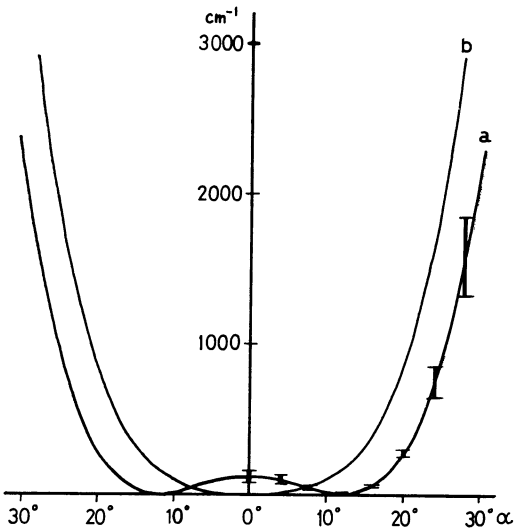

Fig. 3. Potential function for the ν_7 bending vibration in terms of the half bending angle $\alpha=(1/2)[180°-\angle(C=C=C)]$.
(a) Present study (Vertical bar represents random standard uncertainty estimated from the standard deviations in the potential constants a and b given in Table 4.
(b) Potential estimated by Redington (Ref. 10).

43) A. P. Cox, L. F. Thomas and J. Sheridan, *Spectrochim. Acta*, **51**, 542 (1959).
44) A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.*, **13**, 1699 (1959).
45) A. Almenningen, O. Bastiansen and M. Traetteberg, *ibid.*, **15**, 1557 (1961).
46) C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959); B. P. Stoicheff, *Tetrahedron*, **17**, 135 (1962).

tainties.*7

On the other hand, Redington[10] calculated the low-lying energy levels by the WKB method and determined the force constants on the assumption that $\nu_7(n,\ l=0,1\leftarrow 0,0)=63\ cm^{-1}$ and $\nu_7\ (1,1\leftarrow 0,0)=214\ cm^{-1}$. The frequencies of these transitions have not been established, however, because the observed absorption bands are evidently composed of many hot bands ($\Delta l=1$). His potential function shown in Fig. 3, $V(\alpha)=1500\alpha^2+45000\alpha^4$ (cm^{-1}) (the half bending angle α in radians), has no hump and rises moer steeply than the potential determined in the present study.

Centrifugal Effect. A comment should be made on the recent work of Smith.[47] He suggested that the excess in the O_1–O_5 vibrational amplitude observed by Almenningen *et al.*[12] over that calculated by an ordinary method was due to an oscillatory displacement of the nuclei as a result of the centrifugal force generated by the large-amplitude bending motion. If this were the case, the effective force balancing the centrifugal stretching should correspond to the force constants for the C=C and C=O bond stretching, because the centrifugal force acts in the bond direction and is most effective near the zero bending displacement, where the atoms have the largest angular velocities. The effect of the centrifugal force on the O_1–O_5 amplitude, calculated with a set of stretching force constants, turns out to be an order of magnitude smaller than that needed to account for the observed anomaly. Thus the centrifugal force cannot be the essential source of the anomaly. It is not permissible to estimate the centrifugal effect with a much smaller force constant representing "effective stretch-bend interactions" as he assumed in his calculation, because the physical significance of the equation is then lost. As the present analysis has shown, the observed O_1–O_5, O_1–C_4 and C_2–C_4 amplitudes can be explained by a large-amplitude model for the ν_7 vibration.

Statistical Entropy. The entropy due to the ν_7 vibration has been calculated using the potential function determined in the present study. In order to take account of the anharmonicity, the partition function is calculated by a direct summation over all the vibrational levels. The statistical entropy for 230°K and 1 atm is found to be 61.87 cal/deg·mol. This compares with the experimental values,[8] 62.12 ± 0.15 and 61.37 ± 0.11 cal/deg·mol; the ambiguity arises from alternative measurements of the heat of vaporization. According to the recent calculations of Pickett and Strauss,[42] the entropy is insensitive to the various bending potentials which have been suggested to fit the electron-diffraction data.

Infrared Spectra. A series of sharp band heads were observed by Milionis[48] in a high-resolution spectrum in the far-infrared region (20 to 300 cm^{-1}). The spectrum was interpreted in terms of a linear equilibrium structure and a strongly anharmonic vibration with a large increase in the rotational constant B with increasing values of the vibrational quantum number. Since the spectrum was analyzed parametrically, the shape of the potential function for the ν_7 vibration was not determined.

The shape of the ν_7 band has been estimated by the use of the potential function given in Table 4. According to Thorson and Nakagawa,[11] who discussed the characteristic features of the infrared spectrum of a quasi-linear molecule, the band intensities for the bending mode resemble those for a linear molecule, whereas the frequencies approach those for a bent molecule. As the potential hump at the linear position, if present, is estimated to be less than the thermal energy at room temperature, levels above the hump are densely populated. Therefore, the band intensities are calculated by using the band strength S corresponding to the transition in a linear molecule. The band strength is given for a molecule with no nuclear spins by the relation[49]

$$S = K\nu_0[1 - \exp(-h\nu_0/kT)]\,|R|^2 G \exp(-E/kT) \tag{24}$$

where K is a constant, E is the energy of the lower state, R is the transition moment, ν_0 is the transition frequency, and G is a weight factor dependent on the transition (1 for transitions between a Σ-state and any other state, and 2 for all other transitions). The transition moment was calculated by the use of perturbed wavefunctions. The intensities of a series of the transitions $\Delta l=1$, $\Delta n=0$, which are analogous to the "pure rotational spectrum" of a bent molecule, are found to be much stronger than the other transitions. The calculated band contour has its absorption maximum at about 70 cm^{-1}, in contrast to the observed peak around 63 cm^{-1}.[7,48] Both observed and calculated bands have absorption peaks well below 63 cm^{-1}, but the calculated band has much fewer absorption maxima than the observed spectrum. The reason for this discrepancy is unknown. Should the present calculation be responsible for this discrepancy, possible sources are that the n dependence of B has been ignored and that the intensities of the

*7 After the present manuscript had been submitted to this Bulletin, the authors received a preprint from Dr. H. M. Seip (A. Clark and H. M. Seip, *Chem. Phys. Lett.*, **6**, in press (1970)). Their estimate of the potential is in good agreement with that of the present study.

47) W. H. Smith, *Chem. Phys. Lett.*, **3**, 430 (1969).

48) C. C. Milionis, Thesis, Massachusetts Institute of Technology (1969).

49) D. F. Eggers, Jr., and B. L. Crawford, Jr., *J. Chem. Phys.*, **19**, 1554 (1951).

P and R branches have been calculated jointly with those of the Q branches using Eq. (24).

Rotational Constant. The rotational constant B_0 has been determined to be 0.073206 ± 0.00002 cm^{-1} by Lafferty *et al.*[5] from the analysis of a $\sum_g^+ - \sum_g^+$ transition around 3170 cm^{-1}. This constant should be contrasted with the molecular geometry determined in the present study. For a system having a large-amplitude vibration, no theory is available by which one can calculate the "average" rotational constant B_z from B_0*8. If one assumes that the conventional second-order theory is applicable, the B_z constant is calculated from the above B_0 to be 0.07330 cm^{-1}. On the other hand, the average rotational constant can also be estimated from the observed r_g distances provided the approximate procedure of the r_g to r_α^0 conversion[50] is permissible. The B_α^0 constant estimated in this way is 0.0738 ± 0.0002 cm^{-1}. The two constants, B_z and B_α^0, which agree with each other for most nonlinear molecules,[51] thus seem to differ significantly. The origin of this discrepancy is left for a future study.

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*8 *Added in proof:* After the present article was submitted for publication, the following paper has come to our attention: J. T. Hougen, P. R. Bunker and J. W. C. Johns, *J. Mol. Spectry.*, **34**, 136 (1970).

50) K. Kuchitsu, *ibid.*, **49**, 4456 (1968).
51) Y. Morino, K. Kuchitsu and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).

Appendix 1

The constants F and A in Eqs. (12) and (15) are given by the following relations:

$$F = A - B - C + 1/2I_0$$

$$A = m_O[(d_1 - d_2)^2/r_{12} + (d_2 - d_3)^2/r_{23}]^2 + m_C(d_2 - d_3)^4/r_{23}^2$$

where

$$B = 2m_O(r_{12} + r_{23})(d_1 - d_2)^2/r_{12}I_0$$

$$C = 2(d_2 - d_3)^2[m_O(r_{12} + r_{23}) + m_C r_{23}]/r_{23}I_0$$

and other parameters are defined in the text.

Appendex 2

The nonvanishing matrix elements of $q\frac{d}{dq}$ and $q^2\frac{d^2}{dq^2}$ are:

$$\left(\sigma, s \left| q\frac{d}{dq} \right| \sigma + 1, s\right) = -[(\sigma + 1)(\sigma - s + 1)]^{1/2}$$

$$\left(\sigma, s \left| q\frac{d}{dq} \right| \sigma, s\right) = -1$$

$$\left(\sigma, s \left| q\frac{d}{dq} \right| \sigma - 1, s\right) = [\sigma(\sigma - s)]^{1/2}$$

$$\left(\sigma, s \left| q^2\frac{d^2}{dq^2} \right| \sigma + 2, s\right) = [(\sigma + 1)(\sigma + 2)(\sigma - s + 1)(\sigma - s + 2)]^{1/2}$$

$$\left(\sigma, s \left| q^2\frac{d^2}{dq^2} \right| \sigma + 1, s\right) = 3[(\sigma + 1)(\sigma - s + 1)]^{1/2}$$

$$\left(\sigma, s \left| q^2\frac{d^2}{dq^2} \right| \sigma, s\right) = 1 - [(\sigma - s)(2\sigma + 1) + \sigma]$$

$$\left(\sigma, s \left| q^2\frac{d^2}{dq^2} \right| \sigma - 1, s\right) = -3[\sigma(\sigma - s)]^{1/2}$$

$$\left(\sigma, s \left| q^2\frac{d^2}{dq^2} \right| \sigma - 2, s\right) = [\sigma(\sigma - 1)(\sigma - s)(\sigma - s - 1)]^{1/2}$$