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# Radial Matrix Elements and Dipole Moment Function for the Ground State of CO[1]

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Radial matrix elements $\langle vJ|x^k|v'J'\rangle$ for $k = 0$–$5$, $v = 0$–$12$, $|v' - v| = 0$–$4$, and $J$ up to 150 have been calculated for CO using accurate wavefunctions obtained from the numerical solution of the Schrödinger equation with a second-order RKR potential curve. These are used in conjunction with a model dipole moment function (a Padé approximant which has the correct united and separated atom limits and $R^{-4}$ long-range behavior) to analyze the experimental intensity data. For all the levels considered, we conclude that an adequate representation of the dipole moment function is provided by a five-term power series expansion. This simplifies the computation of dipole moment matrix elements, typical results of which are presented to illustrate the dependence on the rotational and vibrational quantum numbers.

## I. INTRODUCTION

Because of its ubiquity, lasing properties, and isotopic richness (*1–4*), carbon monoxide has been one of the most extensively studied molecules. As a result, at the present time, the ground electronic state ($X\ ^1\Sigma^+$) has the most accurate set of experimentally determined vibration–rotation (Dunham) parameters (*5*). Using these frequency data as input, we have computed arrays of radial matrix elements for transitions between a large variety of vibration–rotation levels. These can then be used in conjunction with dipole moment data deduced from an analysis of the comprehensive laboratory intensity data (including results from the pure rotation, fundamental, and first three overtone bands) to calculate dipole moment transition moments. The latter results should be of particular interest to astrophysicists, as they are necessary, for example, in determining

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carbon isotopic ratios (*6*), or computing stellar opacities (*7*). Because of the ambient conditions in these spectral sources (e.g., stars with effective temperatures of several thousand degrees), it is necessary to compute the matrix elements for high values of the vibrational and rotational quantum numbers. As is well known, the direct extrapolation of theoretical expressions valid for low $v$ and $J$ to such high levels can lead to spurious results because of the large influence of vibration–rotation interaction (*8*).

In the present article, we shall first describe the details of the computation of the radial matrix elements. We also present a brief discussion of the form of the dipole moment function, and conclude that, to a high degree of accuracy for all the levels considered, it may be adequately represented by a five-term power series expansion. This form facilitates the computation of dipole transition moments, and allows for future modifications of the dipole moment function (and, hence, transition moments) without recalculating the radial matrix elements. Some typical numerical results are presented in the final section which illustrate the behavior of the dipole matrix elements as functions of vibrational and rotational quantum numbers.

## II. RADIAL MATRIX ELEMENTS

For the ground electronic state of $^{12}C^{16}O$, radial matrix elements, $\langle vJ|x^k|v'J'\rangle$, of the familiar Dunham stretching parameter $x \equiv (R - R_e)/R_e$ have been calculated using "exact" radial wavefunctions obtained by numerical solution of the radial Schrödinger equation. The potential energy curve used in these calculations was obtained from the $E_v$ and $B_v$ data of Mantz *et al.* (*2*) using the second-order RKR procedure of Kirschner and Watson (*9, 10*). To minimize the effect of interpolation uncertainties, turning points were calculated for fractional as well as integral values of the vibrational quantum number $v$ (in steps of 0.1 between $-0.4$ and 1.0 and steps of 0.5 between 1.0 and 37.0). The required equally spaced (in R) integration mesh points were then obtained by seventh-order Lagrangian interpolation.

The radial Schrödinger equation was solved using a version of the Cooley–Cashion (*11, 12*) subroutine SCHR developed by Le Roy (*13*), and the radial matrix element quadratures were performed using Simpson's rule. The range of integration was $0.7 \leq R/R_e \leq 1.75$ and the integration mesh size was $\Delta R = 0.001R_e$, which is sufficiently small to allow for a minimum of 24 mesh points between the closest adjacent nodes of any of the radial eigenfunctions considered. All calculations were performed on an IBM 360/75 computer using double-precision arithmetic. The numerical precision attained is indicated by the fact that the radial wavefunctions for different vibrational levels of a single effective (centrifugally distorted) potential energy curve were orthogonal to better than 0.3 parts in $10^9$. In Jarmain's terminology (*14*), this corresponds to a Franck–Condon "noise factor" of $1 \times 10^{-17}$. This implies that the radial matrix elements described below should all be accurate to within ca. $\pm 1 \times 10^{-9}$. Physical constants entered these calculations only through the single factor (*15*)

$$\hbar^2/(2\mu hc) = 2.45873935 \text{ cm}^{-1}\,\text{Å}^2,$$

while the scaling length $R_e$ was set at $R_e = 1.128322555$ Å.[5]

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[5] Calculated within the Born–Oppenheimer approximation from the experimental $Y_{01}$ (Ref. (*4*)) after making the Dunham corrections (Ref. (*5*)).

The matrix elements $\langle vJ|x^k|v'J'\rangle$ for $k = 0$–5 have been calculated for the levels $v = 0$–12 and $(v' - v) = 0$–4. For each of these 65 vibrational bands, $Q$-branch ($J' = J$; electric dipole forbidden) matrix elements were calculated for $J = 0$–5, and $P$- and $R$-branch ($\Delta J = -1$ and 1, respectively) matrix elements were generated for each $J$ from 0–30, and for every second $J$ from 32–150. The 11 765 sets of radial matrix elements are tabulated band-by-band, with the $Q$-branch results being listed separately. A 208-page listing of these results is on file in the data depository of the *Journal of Molecular Spectroscopy* and can be obtained from the Editor on request.[6] In the following section, we shall indicate how these results can be used to calculate the dipole transition moments.

## III. DIPOLE MOMENT FUNCTION

In order to calculate the dipole moment matrix elements, one must know the dipole moment as a function of internuclear separation. In principle this can be computed with ab initio electronic wavefunctions, but, in practice, with the possible exception of some hydrides (*16*), the results currently available are not as accurate as those which can be deduced from experimental spectral intensities. The most commonly used procedure (*17*) to obtain the dipole moment function experimentally is to assume a power series expansion

$$M(x) = \sum_{i=0} M_i x^i, \tag{1}$$

and to fit the coefficients $M_i$ to the measured rotationless matrix elements $|\langle v0|M(x)|v'0\rangle|$. As discussed elsewhere, the ambiguity in the signs of the experimental values[7] can be removed if one takes into account the effects of vibration–rotation interaction (*17*, *19*). The simple form of Eq. (1) has the advantage that dipole moment matrix elements can be written

$$\langle vJ|M(x)|v'J'\rangle = \sum_{i=0} M_i\langle vJ|x^i|v'J'\rangle, \tag{2}$$

so that future refinements in the dipole moment function do not require a recalculation of the elements of $x^i$.

Using the numerical matrix elements discussed in the preceding section and the best experimental data currently available, which are listed in Table I, one obtains

$$M(x) = -0.12230 + 3.540x - 0.323x^2 - 3.56x^3 + 2.45x^4. \tag{3}$$

This does not differ significantly from results obtained previously (*24*) and, because of the good agreement with most of the experimental intensity data, should provide an adequate representation of $M(x)$ near the minimum of the well.

However, since Eq. (3) diverges for large $x$, other forms which have the correct asymptotic limits can also be considered. In particular, we shall consider the Padé

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[6] These results will be copied onto a requestor's magnetic tape by either of the first two authors (S. M. K. or R. J. L.).

[7] By convention, a negative sign for the permanent dipole moment implies the polarity $C^-O^+$. This polarity has been determined experimentally and confirmed by numerical calculations (*18*). For large $R$ one would expect the polarity $C^+O^-$ so that the simplest possible form is that shown in Fig. 1.

Table I. Experimental Rotationless Dipole Moment Matrix Elements (in Debye)[a]

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$\langle 0|M|0\rangle = -0.10980$ [b]

$\langle 0|M|1\rangle = 1.055 \times 10^{-1}$ [c]

$\langle 0|M|2\rangle = -6.53 \times 10^{-3}$ [d]

$\langle 0|M|3\rangle = 4.24 \times 10^{-4}$ [d]

$\langle 0|M|4\rangle = -2.011 \times 10^{-5}$ [e]

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[a] The relative signs were determined through the experimental J-dependence (Herman-Wallis factors) as discussed in the text.

[b] Ref. (20). The quantity actually measured was $|\langle 0,1|M|0,1\rangle|$ which differs from $\langle 0|M|0\rangle$ by terms of order $(B_e/\omega_e)^2$.

[c] Ref. (21).

[d] Ref. (22).

[e] Ref. (23).

approximant

$$M(x) = \frac{M_0(1 + C_1x + C_2x^2)}{1 + C_3x + C_4x^2 + C_5x^3 + C_\infty x^6}. \tag{4}$$

This form has the correct long-range dependence and limit (*25*) and, by requiring $M(-1) = 0$, it also has the correct united atom limit. The near equilibrium dependence is insensitive to the value of $C_\infty$ (over a reasonable range) and the coefficients $C_i$ can be adjusted to fit either the $\langle v, 0|M(x)|v', 0\rangle$ or the $M_i$ from Eq. (3).

Ignoring the term $C_\infty x^6$ in the denominator and fitting to the $M_i$, one can easily show that

$$\begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ C_4 \\ C_5 \end{bmatrix} = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 \\ M_0 & 0 & -M_0 & 0 & 0 \\ 0 & M_0 & -M_1 & -M_0 & 0 \\ 0 & 0 & -M_2 & -M_1 & -M_0 \\ 0 & 0 & -M_3 & -M_2 & -M_1 \end{bmatrix}^{-1} \begin{bmatrix} 1 \\ M_1 \\ M_2 \\ M_3 \\ M_4 \end{bmatrix}, \tag{5}$$

which leads to the result

$$M(x) = \frac{-0.12230(1 - 27.818x - 28.818x^2)}{1 + 1.126x + 1.128x^2 + 0.544x^3 + C_\infty x^6}. \tag{6}$$

(Within the experimental uncertainties, fitting Eq. (4) with reasonable choices of $C_\infty$

Table II. Dipole Moment Matrix Elements
for $^{12}C^{16}O$ (in Debye)

| J | <0,J\|M\|1,J+1> | <4,J\|M\|5,J+1> | <8,J\|M\|9,J+1> | J | <0,J\|M\|3, J+1> | <4,J\|M\|7,J+1> | <8,J\|M\|11,J+1> |
|---|---|---|---|---|---|---|---|
| 0 | 1.055(-1)[a] | 2.345(-1) | 3.116(-1) | 0 | 4.268(-4) | 2.835(-3) | 6.841(-3) |
| 10 | 1.057(-1) | 2.346(-1) | 3.113(-1) | 10 | 4.529(-4) | 2.991(-3) | 7.182(-3) |
| 20 | 1.059(-1) | 2.347(-1) | 3.111(-1) | 20 | 4.820(-4) | 3.165(-3) | 7.563(-3) |
| 30 | 1.062(-1) | 2.350(-1) | 3.111(-1) | 30 | 5.140(-4) | 3.358(-3) | 7.987(-3) |
| 40 | 1.065(-1) | 2.354(-1) | 3.111(-1) | 40 | 5.495(-4) | 3.572(-3) | 8.457(-3) |
| 50 | 1.068(-1) | 2.358(-1) | 3.111(-1) | 50 | 5.885(-4) | 3.807(-3) | 8.976(-3) |
| 100 | 1.087(-1) | 2.377(-1) | 3.101(-1) | 100 | 8.508(-4) | 5.394(-3) | 1.248(-2) |
| 150 | 1.096(-1) | 2.357(-1) | 3.015(-1) | 150 | 1.286(-3) | 8.024(-3) | 1.736(-2) |

| J | <0,J\|M\|2,J+1> | <4,J\|M\|6,J+1> | <8,J\|M\|10,J+1> | J | <0,J\|M\|4,J+1> | <4,J\|M\|8,J+1> | <8,J\|M\|12,J+1> |
|---|---|---|---|---|---|---|---|
| 0 | -6.546(-3) | -2.650(-2) | -4.775(-2) | 0 | -2.056(-5) | -2.397(-4) | -8.270(-4) |
| 10 | -6.722(-3) | -2.715(-2) | -4.885(-2) | 10 | -2.423(-5) | -2.717(-4) | -9.150(-4) |
| 20 | -6.915(-3) | -2.788(-2) | -5.007(-2) | 20 | -2.834(-5) | -3.076(-4) | -1.014(-3) |
| 30 | -7.127(-3) | -2.868(-2) | -5.140(-2) | 30 | -3.293(-5) | -3.477(-4) | -1.126(-3) |
| 40 | -7.359(-3) | -2.955(-2) | -5.286(-2) | 40 | -3.804(-5) | -3.926(-4) | -1.251(-3) |
| 50 | -7.609(-3) | -3.050(-2) | -5.444(-2) | 50 | -4.374(-5) | -4.428(-4) | -1.391(-3) |
| 100 | -9.181(-3) | -3.641(-2) | -6.429(-2) | 100 | -8.428(-5) | -8.014(-4) | -2.395(-3) |
| 150 | -1.140(-2) | -4.465(-2) | -7.772(-2) | 150 | -1.605(-4) | -1.480(-3) | -4.305(-3) |

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[a] The numbers in parentheses are the appropriate powers of 10.

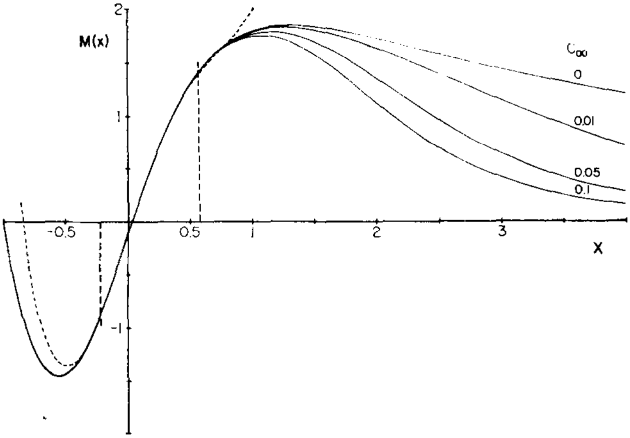

FIG. 1. Model dipole moment function for CO in Debye units. Full lines are Padé approximants with $C_\infty = 0, 0.01, 0.05$, and 0.1; the dashed curve is a five-term power series expansion. The classical turning points for the $v = 30$, $J = 0$ level are indicated by dashed lines.

directly to the experimental $\langle v, 0|M(x)|v', 0\rangle$ leads to the same result.) In Fig. 1 we plot Eq. (6) for several values of the coefficient $C_\infty$ (solid curves) and also Eq. (3) (dashed curve). As expected, these two forms agree quite well over the most significant region around $x = 0$. Indeed, for $v = 30$ (approximately 55 000 cm$^{-1}$ above the well minimum, and corresponding to $x_{\min} \simeq {}^{-}0.217$ and $x_{\max} \simeq 0.572$, indicated by the vertical dotted lines in Fig. 1, the two functions agree to approximately 1% at $x_{\max}$ and to 0.1% at $x_{\min}$. Thus, dipole moment matrix elements (integrals) calculated with either Eq. (3) or Eq. (6) agree with each other to well within the experimental uncertainties.

One final point deserves mention. Within the Born–Oppenheimer framework, the dipole moment function is independent of isotopic substitution. Consequently, in order to generate analogous isotopic dipole moment matrix elements, one has only to recompute the radial matrix elements $\langle vJ|x^i|v'J'\rangle$ for the isotopes or, if less accuracy is warranted, one can see from the theoretical results presented in Ref. (*24*) how these elements scale with the isotopic reduced masses.

## IV. RESULTS AND DISCUSSION

Using the dipole moment function given by Eq. (3) and the numerical radial matrix elements, one can calculate the dipole moment matrix elements for all of the levels mentioned above. Some typical results are presented in Table II which illustrate the dependence on $v$ and $J$. Several trends are immediately discernible: (1) The $\Delta v = 1$ sequence of matrix elements shows very small rotational effects ($\simeq$1% differences between $J = 0$ and $J = 100$). This point has been noted previously (*24*) and is in excellent accord with experiment (*26*). (2) The $J$ dependence becomes more pronounced as $\Delta v$ increases, amounting to as much as a factor of 5 for the higher levels. This behavior agrees with the prediction (*27*) that the magnitude of the $J$ dependence should vary as the difference between the factors $D_v/(B_v)^{\frac{3}{2}}$ for the initial and final states, where $B_v$ and $D_v$ are the usual rotational constants. (3) For a given $\Delta v$, the magnitude of the

$J$ dependence is somewhat comparable. The exact numerical results, however, depend sensitively on $v$ because of cancellation effects [in Eq. (2)] and the changes in sign of some radial matrix elements with increasing $J$.

In conclusion, we would like to mention that the above results for radial matrix elements can be extended to larger $\Delta v$ or to higher $v$ or $J$ levels with almost comparable accuracy. However, in order to calculate the corresponding dipole moment matrix elements, a more realistic dipole moment function would be desirable, especially in the region of the outer turning point. A reasonable procedure would be to fit $C_\infty$ to ab initio results for large internuclear separation where such calculations are relatively more accurate (*28*). Work in this direction is currently in progress.

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