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Calculation of the Vibration-Rotational Transition Moments: Matrix Method

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One version of the matrix method, combination of the analytic representation of wavefunctions and the HEG scheme (J. Chem. Phys. **43**, 1515 (1965)) was used to calculate the vibration-rotational wavefunctions and infra-red transition moments of OH $A\,^2\Sigma^+$ state. Besides introducing this method as an alternative to the numerical integration method, it is shown in this report that the calculated transition moments are virtually independent of the nonlinear parameters of the basis functions. This makes optimization of the parameters unnecessary and facilitates its application. The method is also shown to be very reliable.

Key words: Infra-red transition moments – OH $A^2\Sigma^+$

1. Introduction

Recent years have seen several examples of sophisticated *ab initio* calculation of the vibrational transition moments for diatomic molecules. Those among the latest are the works on LiH by Docken and Hinze [1], on the $X^2\Pi$ state of the radical OH by Mies [2] and another work on the same radical by Chu *et al.* [3]. In these calculations, the radial equation for the nuclear motion is solved numerically and the resultant wavefunctions are used to compute the transition moments, also by the numerical integration method. The numerical process is generally accurate but its intermediate results, such as the vibrational wavefunctions, are extremely cumbersome for handling. Since the knowledge of the vibrational transition probability is needed more and more in various aspects of astronomy, chemical physics and their related technologies, it is important that more practical ways of computing these quantities be explored. This is the purpose of the present study.

All methods of solving eigenvalue equation based on the variational principle and expansion of the eigenfunctions in a basis set can be broadly called the matrix method. Shore [4] has conducted an analysis of the method as applied to the calculation of the molecular vibration and also summarized several versions of the method found among the literature. However, these papers are all concerned with the methodological aspects of the matrix method [5] and the efforts to exploit its potential are peculiarly scarce. The present author has applied the method to a molecular state characterized by a double-minimum potential energy curve [6].

He also successfully adapted the method to the calculation of the Franck-Condon factors [7].

Because of its nature, the matrix method can be expected to be even better suited for the computation of the vibrational transition probability. This paper presents the results of a study on the $A\,^2\Sigma^+$ state of the radical OH.

2. Method

One-dimensional vibrational wavefunction $\psi(v, J)$ is expanded in terms of a set of orthonormal analytic functions $\{\phi_n(\alpha, \beta)\}$ where α and β are parameters.

$$\psi(v, J) = \sum_n c_n(v, J)\, \phi_n(\alpha, \beta) \tag{1}$$

The coefficients $c_n(v, J)$ are obtained from the diagonalization of the Hamiltonian matrix $\boldsymbol{H}$ defined by

$$\boldsymbol{H} = \boldsymbol{T} + \boldsymbol{V} \tag{2}$$

where

$$(\boldsymbol{T})_{kl} = \langle \phi_k | -(2m)^{-1} d^2/dR^2 | \phi_l \rangle \tag{3}$$

$$(\boldsymbol{V})_{kl} = \langle \phi_k | V(R) | \phi_l \rangle \tag{4}$$

$$V(R) = U(R) + [J(J+1) - \Lambda^2]/2mR^2. \tag{5}$$

In these equations, m stands for the reduced mass, R the internuclear distance, $U(R)$ indicates the potential energy, J the total angular momentum and Λ is the axial component of the electronic angular momentum.

The key step of the method used in this work is the evaluation of the matrix **V**. A scheme devised by Harris *et al.* [8] (HEG scheme) enables one to use potential function $U(R)$ in any form, including RKR or *ab initio* potential, in this conjunction. In the HEG scheme one first diagonalizes the matrix $\boldsymbol{R} = \langle \phi_k | R | \phi_l \rangle$ obtaining a set of eigenvalues $\{R'_n\}$:

$$R'_n = (\boldsymbol{U}^{-1}\, \boldsymbol{R}\boldsymbol{U})_{nn} \tag{6}$$

where $\boldsymbol{U}$ is an orthogonal transformation. One can then apply a suitable translation of the origin to define a new set of eigenvalues $\{R_n\}$ related to the set $\{R'_n\}$ by

$$R_n = (C + R'_n)\alpha^{-1/2} \tag{7}$$

where C is a constant. For the reason to be given later it is advantageous to choose the constant C such that the minimum of the new set $\{R_n\}$, $R_{\min}$, is always a small positive number. $V(R_n)$ evaluated at $R = R_n$ and with a specific value of J is substituted for the corresponding diagonal element R'_n to form a diagonal matrix $\boldsymbol{V}^d$:

$$V(R_n) \rightarrow R'_n; \quad (\boldsymbol{V}^d)_{nn} = V(R_n). \tag{8}$$

The desired matrix $\boldsymbol{V}$ is then given by the inverse transformation:

$$\boldsymbol{V} = \boldsymbol{U}\boldsymbol{V}^d\, \boldsymbol{U}^{-1}. \tag{9}$$

Hamiltonian matrix $\boldsymbol{H}$ is formed and diagonalized to yield vibrational energy eigenvalues and eigenfunctions.

Let $\mu(R)$ be the dipole moment of the system. The steps prescribed in Eqs.(8) and (9) are repeated to give the matrix $\boldsymbol{D}$:

$$\mu(R_n) \rightarrow R_n'; \quad (\boldsymbol{D}^d)_{nn} = \mu(R_n) \tag{10}$$

$$\boldsymbol{D} = \boldsymbol{U}\boldsymbol{D}^d\, \boldsymbol{U}^{-1} \tag{11}$$

where

$$(\boldsymbol{D})_{kl} = \langle \phi_k | \mu(R) | \phi_l \rangle. \tag{12}$$

The vibrational transition moment $M(v'', J'' \rightarrow v', J')$ is then given by

$$\begin{aligned} M(v'', J'' \rightarrow v', J') &= \langle \psi(v'', J'') | \mu(R) | \Psi(v', J') \rangle \\ &= \boldsymbol{C}^*(v'', J'')\, \boldsymbol{D}\boldsymbol{C}(v', J') \end{aligned} \tag{13}$$

where $\boldsymbol{C}^*(v'', J')$ is a row vector whose elements are the expansion coefficients of $\psi(v'', J'')$.

3. Calculation and Results

It is self-evident that the vibrational wavefunctions and hence the transition moments can not be calculated with higher certainty and accuracy than those of the potential energy curve and the dipole moment function used in the calculation. Therefore, to avoid any further complication, one should select for test cases those systems for which both $U(R)$ and $\mu(R)$ are known with a high certainty, if not accuracy, over a wide range of R. For this reason, the $A\,^2\Sigma^+$ state of the radical OH is considered in this study since a fairly complete work on this system has recently been published [3].

3.1. Vibrational Eigenvalues and Eigenfunctions

In all computations reported in this paper the vibrational wavefunctions are expanded over a basis set comprising the first 60 harmonic oscillator eigenfunctions $\phi_n(\alpha, R_0)$

$$\phi_n(\alpha, R_0) = (\alpha/\pi)^{1/4}\, (1/2^n n!)^{1/2} H_n(\xi) \exp(-\xi^2/2) \tag{14}$$

with

$$\xi = \alpha^{1/2}(R - R_0)$$

and $H_n(\xi)$ is an Hermite polynomial. Choice of the parameters α and R_0 has been discussed in full detail elsewhere [4–7].

The *ab initio* potential energy and dipole moment of OH computed by Chu *et al.* [3] were fitted to cubic equations of R for interpolation in connection with Eqs.(8) and (10). Calculations were carried out for various values of α ranging from 8.5 to 25.0. It has been demonstrated previously [7] that with a 60-term expansion the resultant eigenvalues and eigenfunctions are for most part sufficiently stationary against the variation of α and R_0 as to render the choice of these parameters noncrucial. Hence, only the results of a representative case, $\alpha = 16.0$, are given.

Table 1. Some Spectroscopic Parameters (in cm^{-1}) OH $A\,{}^2\Sigma^+$

v	$\Delta G_{v+1/2}$			B_v			$D_v \times 10^3$		
	Chu *et al.*	this work[a]	expt.[b]	Chu *et al.*	this work	expt.[c]	Chu *et al.*	this work	expt.[c]
0	2986	2987.3	2988.6	17.04	17.05	16.96	2.08	2.079	2.039
1	2774	2774.0	2793.0	16.15	16.14	16.13	2.09	2.082	2.024
2	2572	2575.3	2593.5	15.29	15.29	15.28	2.07	2.055	2.027
3	2350	2354.3	2385.5	14.40	14.40	14.42	2.13	2.096	2.067
4	2079	2071.0		13.41	13.40		2.35	2.433	

[a] $\alpha=16.0$, $J=0.5$. Potential curve from Chu *et al.*: J. Chem. Phys. **61**, 5389 (1974)

[b] Carlone,C., Dalby,F.W.: Can. J. Phys. **47**, 1945 (1969)

[c] Moore,E.A., Richards,W.G.: Phys. Scr. **3**, 223 (1971)

Molecular energy level $\varepsilon_{v,J}$ is written as

$$\varepsilon_{v,J}=\varepsilon_v+J(J+1)B_v-J^2(J+1)^2D_v \tag{15}$$

where ε_v indicates the vibrational term. Rotational constants B_v and D_v are computed from three values of $\varepsilon_{v,J}$ with $J=0.5$, 1.5 and 2.5.

3.2. Transition Moments

Since the matrix $\boldsymbol{R}$ has already been diagonalized while computing the molecular energy, the calculation of the matrix $\boldsymbol{D}$ in Eq.(11) requires only interpolations of $\mu(R)$ and multiplication of three matrices. Eq.(13) then gives the transition moment.

Table 2 presents the vibrationally-averaged dipole moment of all calculated bound levels ($v=0$–8) versus the parameter α ranging from $\alpha=8.5$ to $\alpha=25.0$. It is obvious from this table that except the highest bound state, the vibrationally-averaged dipole moments remain, for all practical purposes, virtually constant against α.

Table 2.[a] $\langle\psi(v,J)|\mu(R)|\psi(v,J)\rangle$ versus α–OH $A\,{}^2\Sigma^+$

$v \backslash \alpha$	8.5	10.0	12.0	16.0	25.0
0	0.7375	0.7377	0.7377	0.7376	0.7376
1	0.7749	0.7749	0.7749	0.7750	0.7749
2	0.7994	0.7993	0.7993	0.7993	0.7993
3	0.8116	0.8119	0.8117	0.8117	0.8118
4	0.8072	0.8069	0.8068	0.8068	0.8069
5	0.7751	0.7749	0.7748	0.7748	0.7748
6	0.7000	0.7001	0.7001	0.7000	0.7000
7	0.5501	0.5502	0.5505	0.5505	0.5516
8[b]	0.2916	0.2916	0.2923	0.2955	0.3780

[a] $J=0.5$. All entries in a.u.

[b] Ten bound states are experimentally established. However, the *ab initio* potential contains only nine bound states. See also Chu *et al.*: J. Chem. Phys. **61**, 5389 (1974)

Table 3. Calculated transition moments[a] *vs.* α–$\psi(v, J=0.5) \rightarrow \psi(v+\Delta v, J=1.5)$ OH $A^2\Sigma^+$

α	$\Delta v=1$			$\Delta v=2$			$\Delta v=3$		
v	10.0	12.0	16.0	10.0	12.0	16.0	10.0	12.0	16.0
0	0.0827	0.0827	0.0827	0.0205	0.0205	0.0205	0.0031	0.0031	0.0031
1	0.1037	0.1037	0.1037	0.0377	0.0377	0.0377	0.0078	0.0078	0.0078
2	0.1059	0.1060	0.1060	0.0558	0.0558	0.0558	0.0155	0.0154	0.0154
3	0.0910	0.0911	0.0911	0.0739	0.0739	0.0739	0.0277	0.0277	0.0277
4	0.0552	0.0553	0.0552	0.0859	0.0860	0.0860	0.0443	0.0443	0.0443
5	0.0055	0.0054	0.0054	0.0753	0.0755	0.0756	0.0481	0.0482	0.0486
6	0.0870	0.0867	0.0866	0.0174	0.0176	0.0179	—[b]	—	—
7	0.1486	0.1486	0.1496	—[b]	—	—	—	—	—

[a] For convenience, absolute values (in a.u.) of the moments are listed.

[b] Since only nine bound states are contained in the *ab initio* potential these are not defined.

Table 3 shows part of the R-branch ($J''=0.5 \rightarrow J'=1.5$) of the transition moment matrix $\boldsymbol{M}$.

4. Discussion

While the theoretical potential curve of Chu *et al.* [3] should not be far from the limit of accuracy an *ab initio* calculation on a system of this size can normally attain at the present time, it is still considerably different from the RKR potential [9]. As can be seen in Table 1, the calculated vibrational quanta $\Delta G_{v+\frac{1}{2}}$ show a rapidly increasing deviation from the experimental results with the quantum number v. Moreover, the *ab initio* potential is found, both in this calculation and in the work of Chu *et al.*, [3] to accommodate nine bound levels as compared to ten as experimentally determined.

Since an *ab initio* potential is used, and the aim of this work is to test the matrix method, it is meaningful only to compare the results of the present calculation with those of the numerical integration method. As one can clearly see in Table 1, the agreement between the results of these two methods is generally very satisfactory. One also notices, at a closer inspection, that the agreement is considerably better for the rotational levels than for the vibrational quanta. This latter point is explained in the following paragraph.

As defined in Eq.(5), the potential function $V(R)$ for the vibration-rotation motion consists of the purely vibrational part $U(R)$ and rotational part $[J(J+1)-\Lambda^2]/2mR^2$. In setting up the matrix V^d defined in Eq.(8), one evaluates $U(R_n)$ by interpolation and adds the rotational part, evaluated by a simple substitution of R by the value R_n. In the numerical integration procedure, one also interpolates $U(R)$ at every integration step and computes the rotational part by a simple substitution. This is the only step in both methods where vibration and rotation are treated differently. To interpolate any function from a set of finite number of points is always subject to numerical error, no matter how small. Hence, it is conceivable that the present calculation and the one by Chu *et al.* [3] produced different, albeit only very slightly, sets of interpolation formulas from the same potential $U(R)$, resulting into a small disagreement between the calculated vibrational levels. In most cases, the potential energy $U(R)$ is computed less densely at the range of R farther removed from the equilibrium distance. This, in turn, can lead to higher uncertainties in the interpolation and, consequently, to a greater deviation in the higher vibrational levels, as seen in Table 1. This explanation is also supported by previous calculations [7] which showed the matrix method to be most accurate where the potential energy curves are known in more detail. In contrast, the evaluation of the part $[J(J+1)-\Lambda^2]/2mR^2$ by a simple substitution $R=R_n$ cannot introduce any additional error. Therefore, the rotational structure should be more easily reproducible by two independent calculations. One can conclude from the above reasoning that the small discrepancy shown by these two calculations are probably due to the numerical errors in the interpolation of $U(R)$ but not due to factors inherent to the methods.

The vibrationally-averaged dipole moments given in Table 2 are surprisingly stable inspite of the drastic change of α. Since the vibrational wavefunctions are expanded in terms of the harmonic oscillator eigenfunctions which are explicit functions of α, one might expect the wavefunctions to vary with this parameter. On the contrary, the dipole moment function $\mu(R)$ is independent of α. Hence, even a small phase shift of the wavefunction along the R-axis would likely become reflected in the average dipole moment. Not to mention if the variation of α causes any change in the functional form of the wavefunctions. However, this situation is not seen except in the bottom row. Therefore, the excellent stability for $v\leqslant 7$ should be inferred as an indication that the corresponding wavefunctions remain practically unchanged by the variation of α over this range. In other words, the choice of the parameter α is not crucial for the calculation described in this paper.

Let $R_{\max}$ represent the maximum of the set $\{R_n\}$ defined in Eq.(7). It has been pointed out [5] that the HEG scheme is equivalent to the Gaussian quadrature, with the set $\{R_n\}$ serving in the procedure as nothing other than a set of unevenly spaced quadrature points. It follows that the scheme is responsible [10] only in the region of R spanned by $R_{\min}$ and $R_{\max}$. Outside this region, the accuracy of the scheme is entirely determined by the amenability of the functions, $U(R)$ and $\mu(R)$, to extrapolation.

In the present calculation it is arbitrarily set $R_n=(R'_{\max}+R'_n)\alpha^{-1/2}$. For the 60-term basis set $\{\phi_n\}$, $R'_{\max}=-R'_{\min}\approx 10$ a.u. One can roughly estimate the value of $R_{\max}$, and thus the region where the HEG scheme is reliable, as a function of α. Now, according to the *ab initio* potential energy, the highest bound level $v=8$ has its larger of the classical turning points at $R\approx 4.8$ a.u. One can readily see that at $\alpha=25$, $R_{\max}$ falls well short of this turning point. As α decreases, $R_{\max}$ increases, becoming roughly comparable to 4.8 a.u. at $\alpha=16$. At smaller values of α the range extends farther down to the large R. As a result the energy and wavefunction of this level change quite drastically as α is varied from $\alpha=25$ to $\alpha=12$. Beyond the latter value these quantities become reasonably constant. This explains the fluctuation of the entries in the bottom row and also the deviation of the last entry for $v=7$ from others in the same row.

The transition moments listed in Table 3 involve both vibrational and rotational excitations: $v\rightarrow v+\Delta v$, $J=0.5\rightarrow J=1.5$. Nonetheless, one also finds these matrix elements to be very stationary against α, although over a narrower range of the parameter. As in the averaged dipole moments, only those transitions involving the highest bound level $v=8$ are significantly affected, up to 3%, by the variation of α. All other transition moments change, to a maximum of a half percent when α is varied from $\alpha=10.0$ to $\alpha=16.0$.

One can thus infer from Tables 2 and 3 that as long as the value assumed for the parameter α is not as extreme as to severely limit the validity of the HEG scheme, the vibrational wavefunctions are remarkably independent of this parameter. The need to search for the optimal value of any nonlinear parameters always hampers the usefulness of a computational scheme: the narrower is the range of the optimal value so is the usefulness of the method. The remarkable independence of the results displayed in these tables thus ensures the facility of application.

Since Chu *et al.* [3] published only two values from the results of their calculation by the numerical integration method, comparison can be but very limited. Their reported vibrationally-averaged dipole moments for the levels $v=0$ and $v=1$ are 0.738 and 0.774, respectively, as compared to 0.738 and 0.775, also in the same order, of the present calculation. Although limited, these figures are in line with the spectroscopic constants shown in Table 1.

It is interesting to observe that the behaviour of the transition moments versus the initial vibrational quantum number v in Table 3 shows a general resemblance with the similar ones of Mies [2]. The magnitude of the moment for the vibrational fundamental $\Delta v=1$ reaches a maximum at $v=2$, becomes nearly zero at $v=5$ before it changes sign and increases very rapidly towards the vibrational continuum.

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