

Derivation of Accurate Kinetic and Potential-energy Functions for Several Simultaneous Large-amplitude Vibrations: Application to Acetaldehyde in the S_0 and T_1 States

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A procedure is presented for deriving kinetic and potential-energy functions from experimental data for an arbitrary number of large-amplitude vibrations. As a starting point, the method requires a high-quality estimate of the spectroscopic data. We use the previously developed technique of spectrum generation from *ab initio* calculations to obtain the initial kinetic and potential functions. The present technique minimizes the error between the calculated and experimental energy levels by considering both the kinetic and potential terms. The application to the internal rotation of the methyl group in the S_0 state of acetaldehyde shows that the technique is capable of yielding agreement to the experimental measurements to within 0.0001 cm^{-1} . The joint methyl torsion and aldehyde wagging modes for the T_1 state of acetaldehyde are also considered. From the two-dimensional potential function the barriers to methyl rotation and to inversion of the aldehydic hydrogen are found to be 633.60 and 935.76 cm^{-1} , respectively. The equilibrium conformation obtained from the two-dimensional potential shows one methyl hydrogen almost eclipsing the aldehydic oxygen (torsion angle 186.40°) whereas the aldehydic hydrogen distorts out of the molecular frame by 39.17° . These structural results are found to differ from that obtained using one-dimensional models, but they agree very well with the results of *ab initio* calculations.

In the usual harmonic approximation, the vibrational modes of a molecule are assumed to be of small amplitude and are uncoupled from each other. In this case, the kinetic energy depends on the static equilibrium molecular geometry and is considered to be constant in the refinement of the force field. Experimental force constants are obtained by the classical refinement of the force field through a least-squares procedure.^{1–3} The development of a similar treatment for large-amplitude variations is complicated by the interactions between the modes. As the kinetic contributions to the hamiltonian are no longer constant for this case,⁴ they must be included in the refinement process.

The presence of potential-energy barriers is characteristic of molecular systems that undergo intermolecular large-amplitude motion. The effects of the barriers are directly observed as a splitting of the energy levels in the vibrational spectrum. It is from the experimentally derived large-amplitude vibrational energy levels that the potential-energy surfaces are determined. These surfaces contain information about the equilibrium conformations and barrier heights. The accuracy of the experimentally derived structural and dynamic information depends on the assumptions in the underlying theory employed in the interpretation of the data.

In this paper we develop a theoretical treatment for determining reliable kinetic and potential functions for several coupled large-amplitude vibrations from experimental data. The starting point for the technique is a procedure that we have recently developed for studying large-amplitude vibrations.⁵ The method is applied to methyl torsion in the S_0 ground electronic state of acetaldehyde using the recent experimental results for the $\nu = 1$ and 2 torsional energy levels.⁶ The effect of a variable kinetic energy term is analysed and the barrier to rotation is compared with previous derivations. In addition, the two-dimensional problem of torsion-wagging in the T_1 triplet state of acetaldehyde is considered.

Theory

The objective is to minimize the difference between the n_e

experimental values for n large-amplitude vibrational energy levels, ϵ_i^e , and the corresponding calculated vibrational levels, ϵ_i^c . Thus, we construct an auxiliary function $f(C)$ that represents the total difference and is defined as

$$f(C) = \sum_i^{n_e} (\epsilon_i^e - \epsilon_i^c)^2 \quad (1)$$

Therefore, the problem is reduced to the minimization of the $f(C)$ function. The hamiltonian used for the large-amplitude motions has been derived previously.⁵ This hamiltonian uses a potential and kinetic part expanded in a Fourier series on the n large-amplitude vibrational coordinates, q_1, \dots, q_n . Thus, the potential function is expressed as

$$V = \sum_k^{N_V} V_k^0 \chi_k(q_1, \dots, q_n) \quad (2)$$

where N_V and the V^0 s represent the number of terms and the coefficients in the expansion, respectively.

For the kinetic part we have

$$\hat{T} = \sum_i^n \sum_j^n \left[B_{ij} \frac{\partial^2}{\partial q_i \partial q_j} + \left(\frac{\partial B_{ij}}{\partial q_i} \right) \frac{\partial}{\partial q_j} \right] \quad (3)$$

where the B_{ij} s are kinetic terms obtained from the rotational-vibrational G matrix.^{7,8} These terms are also expanded in a Fourier series,

$$B_{ij} = \sum_k^{N_B} B_{ijk}^0 \chi_k(q_1, \dots, q_n) \quad (4)$$

where N_B represents the number of terms in the expansion. χ_k in eqn. (2) and (4) is a product of n trigonometric functions, one for each vibration

$$\chi_k = \prod_k^n f(q_k) \quad (5)$$

with

$$f(q_k) = \begin{cases} \cos(Kq_k); & K = 0, 1, \dots \\ \sin(Kq_k); & K = 1, 2, \dots \end{cases} \quad (6)$$

The hamiltonian is solved variationally in the basis of the trigonometric normalized free rotor functions.

The eigenvalues ε_i^j in eqn. (1) are obtained through eqn. (2) and (3). Thus, eqn. (1) depends on the B_{ijk}^0 and V_k^0 terms. The minimization of $f(C)$ can be carried out using vectorial notation. Thus, C in eqn. (1) is defined as a column vector formed by the B_{ijk}^0 and V_k^0 coefficients of eqn. (2) and (4) except for the constant-potential term V_1^0 that is dependent on the other potential terms. The value of $f(C)$ in the neighbourhood, C_1 , of a certain point C can be obtained by expanding in a Taylor series,

$$f(C_1) = f(C) + g^+ \cdot q + (1/2)q^+ \cdot h \cdot q + \dots \quad (7)$$

where

$$g^+ = [\partial f(C)/\partial C_1, \dots, \partial f(C)/\partial C_n] \quad (8)$$

is the transpose vector of derivatives, the gradients,

$$q = C_1 - C \quad (9)$$

is the vector of increments and h is the hessian matrix. The hessian is formed by the second derivatives and its non-diagonal terms reflect the interdependence between the kinetic and potential terms. The gradient at the point C_1 can be expressed as

$$g(C_1) = g(C) + h \cdot q(C) + \dots \quad (10)$$

Assuming C_1 to be a minimum, $g(C_1) = 0$ and eqn. (10) yields

$$C_1 = C - h^{-1} \cdot g(C) \quad (11)$$

Eqn. (11) is exact for a quadratic form and can be used as the basis to locate the minimum of eqn. (1). Thus, for two successive approximations C_n and C_{n+1} we obtain

$$C_{n+1} = C_n - h(C_n)^{-1} \cdot g(C_n) \quad (12)$$

The equation (12) represents a Newton-like method for gradiental minimization.⁹ The minimization procedure can be enhanced using

$$C_{n+1} = C_n - \alpha \cdot h(C_n)^{-1} \cdot g(C_n) \quad (13)$$

where α is a parameter that gives the function minimum along the search direction defined by $h(C_n)^{-1}g(C_n)$. The parameter is obtained using a line-search procedure for each minimization iteration.¹⁰

The gradient with respect to one of the kinetic or potential terms, C_j , is obtained from eqn. (1) as

$$(\partial f/\partial C_j) = 2 \sum_i^{n_e} (\varepsilon_i^j - \varepsilon_i^0) \cdot (\partial \varepsilon_i^j/\partial C_j) \quad (14)$$

whereas for the jk element of the hessian matrix we get

$$(\partial^2 f/\partial C_j \partial C_k) = 2 \sum_i^{n_e} (\partial \varepsilon_i^j/\partial C_j) \cdot (\partial \varepsilon_i^j/\partial C_k) \quad (15)$$

Eqn. (14) and (15) can be evaluated after calculation of the elements involving the derivatives of the eigenvalues, *i.e.* the energy gradients. Thus, we define an auxiliary matrix, A , whose ij element is given by

$$A_{ij} = (\partial \varepsilon_i^j/\partial C_j) \quad (16)$$

The matrix A has n_e rows and m columns. Using A , the components of the gradient vector and the hessian matrix can be obtained from eqn. (14) and (15) as

$$g_j = 2 \sum_i^{n_e} (\varepsilon_i^j - \varepsilon_i^0) \cdot A_{ij} \quad (17)$$

$$h_{ij} = 2 \sum_i^{n_e} A_{ij} \cdot A_{ik}$$

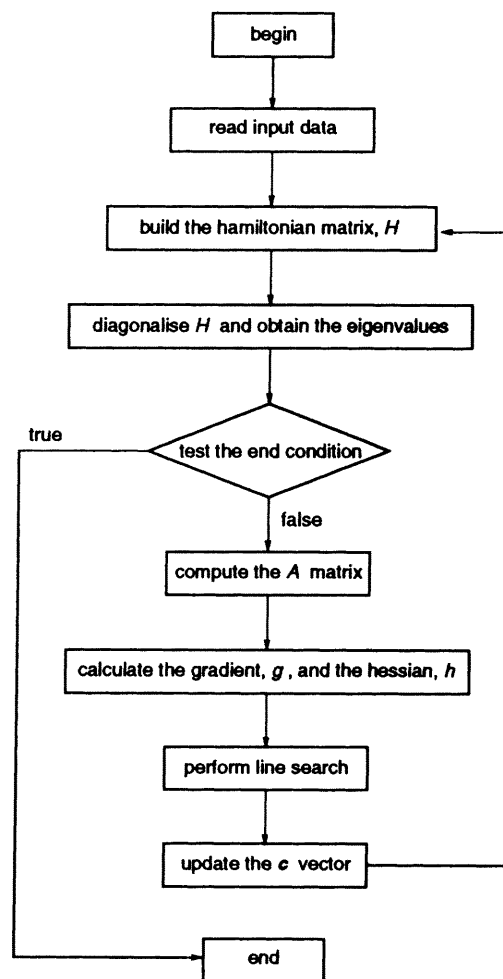


Fig. 1 Flow chart of the fitting procedure

When $n_e = 1$, the hessian is obtained as the product of the column energy gradient vector by its transpose. Thus, the hessian is a singular matrix and the minimization procedure is not applicable.

After some numerical work we found that a good scheme for the location of the minimum is to start with a pseudo-alternating variables technique.⁹ Thus, in the first iteration only the potential terms are affected whereas in the second, the procedure acts only on the kinetic part. In the following iterations the kinetic and potential terms are considered together. Fig. 1 shows the flow chart for the fitting procedure.

Applications

As a first example, we apply the fitting procedure to the S_0 state of acetaldehyde. In the ground electronic state of acetaldehyde, the internal rotation of the CH_3 methyl group against the CHO molecular frame is the single large-amplitude normal mode Q_{15} . This one-dimensional case is well suited for analysing the effects of a variable kinetic term, B_θ , on the barrier to rotation. The energy levels for this case can be classified under the operations of the G_6 group that is isomorphic to the C_{3v} point group. We start with the one-dimensional potential and kinetic functions obtained previously¹¹ from *ab initio* calculations at the MP2/6-311 (d, p) level. These potential and kinetic energy expressions use a $\cos(3\theta)$ term for representing the dependence on the torsional angle, θ , and a $\cos(6\theta)$ term for including the coupling with the remaining $3N - 6$ vibrations.¹² In addition, a com-

Table 1 Fitted energy levels in the S_0 state of acetaldehyde for constant and variable kinetic terms (all values in cm^{-1})

v_{15}	sym	calc. ^a	calc. ^b	calc. ^c	obs. ^d
0	a_1	0.000	0.000	0.0000	0.0000
	e	0.0680	0.0685	0.0685	0.0690
1	e	141.9976	141.9935	141.9935	141.9935
	a_2	143.7392	143.7434	143.7434	143.7434
2	a_1	255.2235	255.2243	255.2243	255.2243
	e	269.1130	269.1121	269.1121	269.1121
3	e	348.9150	349.2337	349.2345	—
	a_2	408.0267	408.2477	408.2575	—
4	a_1	424.9456	425.5432	425.5324	—
	e	508.3805	508.9440	508.9423	—

^a Starting kinetic and potential functions taken from ref. 11: $B_\theta = 7.6437 \text{ cm}^{-1}$, $V = 205.86 - 207.62 \cos(3\theta) + 1.76 \cos(6\theta)$. ^b Starting kinetic and potential functions taken from ref. 11: $B_\theta = 7.6437 + 0.0305 \cos(3\theta) + 0.0037 \cos(6\theta)$, $V = 205.86 - 207.62 \cos(3\theta) + 1.76 \cos(6\theta)$. ^c Starting kinetic and potential functions taken from ref. 13: $B_\theta = 7.5666 \text{ cm}^{-1}$, $V = 395.95 - 203.95 \cos(3\theta) + 6.30 \cos(6\theta) - 0.325 \cos(9\theta)$. ^d Pure torsional energy levels, ref. 6.

parison will be made to the most recent determination of the kinetic and potential function¹³ that uses a constant kinetic energy term and an additional $\cos(9\theta)$ term in the potential function. For the experimental data, we use the most recent determination for the $v_{15} = 1$ and 2 energy levels that have been derived from far infrared and microwave measurements.⁶

Table 1 collects the energy levels obtained from the fitting procedure. Case a corresponds to the constant kinetic energy term and case b to the variable kinetic term. In both cases the first two iterations in the minimization were able to place the difference between each calculated and experimental level to 0.1 or 0.01 cm^{-1} . For the constant kinetic term, the optimization procedure yields calculated levels in agreement with the experimental values to two decimal places. No additional enhancements could be achieved since the gradients were too small for additional improvements. When the variable kinetic energy term was considered, case b, the difference between each calculated and experimental energy level was 10^{-4} cm^{-1} . Case c collects the results obtained by optimizing to four decimal places the energy levels obtained with the latest determined kinetic and potential terms.¹³ In this case, the kinetic part is constant and the potential function has an additional $\cos(9\theta)$ term. However, the results are equivalent to case b. Table 2 gives the kinetic and potential function data for the three cases as well as the barriers to rotation. For the constant kinetic term the barrier is found to be 407.49 cm^{-1} . When the kinetic term is considered to be variable, the barrier is found to be 408.76 cm^{-1} whereas for the case of the

Table 2 Energy barrier, kinetic and potential functions for the methyl rotation in the S_0 state of acetaldehyde obtained by fitting to the experimental values for the $v = 1$ and 2 torsional levels (all values in cm^{-1})

term	B^a	V^a	B^b	V^b	B^c	V^c
constant	7.5523	197.93	7.5643	197.26	7.5664	197.98
$\cos(3\theta)$	—	-203.74	-0.0060	-204.24	—	-203.93
$\cos(6\theta)$	—	5.82	0.0868	6.98	—	6.23
$\cos(9\theta)$	—	—	—	—	—	-0.28
barrier/ cm^{-1}	—	407.49	—	408.48	—	408.43

^a Using a constant kinetic term, case a of Table 1. ^b Using a kinetic term variable with the torsion angle and including the coupling with the remaining vibrations, case b of Table 1. ^c Optimized result from the data of ref. 13, case c of Table 1.

constant kinetic terms with the additional $\cos(9\theta)$ term in the potential the barrier is 408.43 cm^{-1} . The present results show that the change of the methyl kinetic term (B) resulting from the torsion and the coupling with the remaining vibrations have a small but significant effect on the value of the barrier to rotation. The equivalence between the variable kinetic model and the fixed kinetic model with an enhanced potential function is a consequence of the interdependence between the kinetic and potential terms. This fact is reflected in the off-diagonal elements of the hessian matrix which are non-zero. This effect is similar to the inclusion of kinetic pseudo-potential terms in the potential function in the derivation of the hamiltonian for large-amplitude vibrations.^{7,8}

Of somewhat more interest is the use of the fitting procedure to study several large-amplitude motions simultaneously. The T_1 electronic state of acetaldehyde is a suitable test case. In the ground electronic state, acetaldehyde adopts a conformation in which an in-plane hydrogen eclipses the oxygen atom. In the upper T_1 state, the methyl group rotates to an antieclipsed conformation while the aldehydic hydrogen distorts from the plane.¹⁴ In this excited state acetaldehyde shows two coupled large-amplitude vibrations, the rotation of the methyl group, Q_{15} mode, and the wagging of the carbonyl hydrogen, Q_{14} mode. As in the S_0 state the energy levels can be classified under the G_6 non-rigid group.

The $S_0 \rightarrow T_1$ electronic spectrum is the source for the experimental study of the structure of the first triplet state of acetaldehyde, but the experimental study is complicated by the long lifetime of the T_1 state. Thus, our technique will be used to gain additional information on this excited state. Two experiments have been reported covering some aspects of the problem.^{15,16} These spectra are very congested and ill resolved and in their interpretation it has proved useful to use the theoretically simulated spectrum.¹¹ The, two-dimensional, torsion+wagging, potential and kinetic functions that were obtained from the MP2/6-311G(d, p) *ab initio* calculation¹¹ will be used as a starting point for the fitting.

As a starting point, a one-dimensional model for torsion was used to derive the one-dimensional torsional barrier. This model considers variable kinetic and potential functions including a $\cos(6\theta)$ term. Table 3 collects the energy of the $v_{15} = 0, 1, 2$ and 3 levels obtained from the one-dimensional fit of the $v = 1$ and 2 experimental values to the torsional energy levels. The fitted kinetic and potential functions are shown in Table 4. The value for the barrier to methyl rotation is 581.79 cm^{-1} . This is smaller than the 624.80 cm^{-1} value found in ref. 15 that needs a constant kinetic term and a potential function without the $\cos(6\theta)$ term. In addition, the present result differs from the 590 cm^{-1} found in ref. 16 where the $\cos(6\theta)$ term is included in the potential but where the kinetic term is constant and is left out of the fit. It is clear,

Table 3 Torsional energy levels (in cm^{-1}) for the T_1 state of acetaldehyde

v_{15}	sym	calc. ^a	obs. ^b
0	a_1	0.0	0.0
	e	0.02	0.0
1	e	179.8	179.8
	a_2	180.4	—
2	a_1	334.3	334.3
	e	341.4	—
3	e	446.2	—
	a_2	498.2	—

^a The starting kinetic and potential terms have been obtained from the two-dimensional model of ref. 11: $B = 7.7734 + 0.4839 \cos(3\theta) + 1.5629 \cos(6\theta)$, $V = 205.86 - 207.62 \cos(3\theta) + 1.76 \cos(6\theta)$. ^b Ref. 15.

Table 4 Barrier, kinetic and potential functions for the methyl rotation in the T_1 state of acetaldehyde obtained by fitting to the experimental values for the $v = 1$ and 2 torsional levels (all values in cm^{-1})

term	B_θ	V_θ
constant	7.9845	-296.59
$\cos(3\theta)$	0.0052	290.87
$\cos(6\theta)$	-0.0131	5.72
barrier/ cm^{-1}		581.74

however, that the value of the barrier to rotation decreases with the flexibility of both the kinetic and the potential terms.

In a similar way, a one-dimensional model for the wagging is derived from the previous two-dimensional model. Thus, the 531.8 and the 888.4 cm^{-1} experimental energy levels¹⁶ assigned to $v_{14} = 2$ and 3, respectively, are used in the procedure. Table 5 collects the energy levels and Table 6 the resulting kinetic and potential functions. These results were obtained through our variational technique where the dependence of the kinetic and potential terms on the wagging coordinate, α angle, is taken into account by a Fourier-series expansion. In the present case, the number of iterations needed to reduce the difference between the calculated and experimental energy levels to $<0.1 \text{ cm}^{-1}$ increases greatly. This fact can be attributed to the use of a Fourier expansion to represent the wagging. Since the physical behaviour of the potential is not directly represented by the Fourier expansion it is necessary to use more iterations than in the case of the torsion. The one-dimensional inversion barrier is 1198.31 cm^{-1} , which is higher than the 968.1 cm^{-1} found by *ab initio* calculations.¹¹ The minimum of the potential function corresponds to a conformation where the aldehydic hydrogen is distorted by 41.40° from the C—C=O molecular frame of acetaldehyde. This value is in relatively good agreement with the 39.66° angle obtained by *ab initio* computations at the MP2/6-311G(d, p) level.¹¹

Table 5 Wagging energy levels (in cm^{-1}) for the T_1 state of acetaldehyde; the symmetry refers to the inversion of the wagging angle

v_{15}	sym.	calc. ^a	obs. ^b
0	a_1	0.00	0.00
	a_2	0.04	—
1	a_1	526.9	—
	a_2	531.7	531.8
2	a_1	888.3	888.4
	a_2	981.3	—

^a The starting kinetic and potential terms have been obtained from the two-dimensional model of ref. 11: $B = 18.92620 + 1.89022 \cos(2\alpha) + 0.19225 \cos(3\alpha)$, $V = 6584.54 - 7088.89 \cos(\alpha) + 83.21 \cos(2\alpha) + 1632.88 \cos(3\alpha)$. ^b Ref. 16.

Table 6 Inversion barrier, kinetic and potential functions for the aldehyde hydrogen wagging in the T_1 state of acetaldehyde obtained by fitting to the experimental values for the $v_{14} = 1$ and 2 inversion levels (all values in cm^{-1})

term	B_α	V_α
constant	11.3598	7360.83
$\cos(\alpha)$	—	-8568.59
$\cos(2\alpha)$	-2.3420	609.49
$\cos(3\alpha)$	-2.8345	1796.58
barrier/ cm^{-1}		1198.31

Table 7 Torsional and wagging energy levels (in cm^{-1}) for the T_1 state of acetaldehyde

v_{15}	v_{14}	sym.	calc.	obs.
0	0	a_1	0.00	0.00 ^a
		e	0.02	0.00 ^a
1	0	e	179.7	179.8 ^b
		a_2	180.2	
2	0	a_1	334.4	334.3 ^b
		e	339.1	
3	0	e	460.0	
		a_2	493.0	
0	1	a_2	5.5	
		e	5.5	
1	1	e	181.3	
		a_1	181.6	
2	1	a_2	336.0	
		e	340.3	
3	1	e	464.1	
		a_1	488.9	
0	2	e	531.2	
		a_1	531.9	531.8 ^c
1	2	e	736.1	
		a_2	738.2	
2	2	a_1	886.2	
		e	888.3	888.4 ^c

^a Not directly observed. ^b Ref. 15. ^c Ref. 16.

Table 8 Fitted kinetic and potential functions and torsional and inversion barriers for the T_1 state of acetaldehyde (all values in cm^{-1})

term	$V(\theta, \alpha)$	B_θ	B_α	$B_{\alpha\alpha}$
constant	6966.82	7.8938	18.6617	-3.8590
$\cos(\alpha)$	-7547.01	—	—	0.0102
$\cos(2\alpha)$	—	1.4223	2.2429	—
$\cos(3\alpha)$	1722.73	0.0267	-0.1550	-0.4875
$\cos(3\theta)$	315.78	-0.9512	0.3648	0.1022
$\cos(6\theta)$	2.25	—	—	—
$\cos(3\theta)\cos(\alpha)$	—	2.0275	—	0.3730
$\cos(3\theta)\cos(2\alpha)$	-70.23	1.5816	-0.0433	—
$\cos(3\theta)\cos(3\alpha)$	-32.92	—	0.0743	-0.9923
$\cos(6\theta)\cos(\alpha)$	—	0.6215	—	0.6777
$\sin(3\theta)\sin(\alpha)$	-137.18	-6.2751	-0.3674	0.3624
$\sin(3\theta)\sin(2\alpha)$	68.77	4.4102	—	—
$\sin(3\theta)\sin(3\alpha)$	87.90	—	-0.0512	-0.5214
torsional barrier/ cm^{-1}	633.60			
inversion barrier/ cm^{-1}	935.76			

Using our two-dimensional theoretical spectrum¹¹ it is possible to correlate the $v_{14} = 2$, $v_{15} = 2$ energy level calculated at 881.53 cm^{-1} with the 888.4 cm^{-1} experimental value.¹⁶ In addition, a comparison of the theoretical† with experimental data identifies the calculated $v_{14} = 2$, $v_{15} = 0$, energy level at 536.7 cm^{-1} with the 531.8 cm^{-1} observed energy level. Table 7 shows the energy levels obtained after fitting to 0.1 cm^{-1} of the experimental data. Table 8 shows the resulting kinetic and potential functions as well as the torsion and inversion barriers. The torsional barrier is found to be 633.60 cm^{-1} . Thus, the effect of the wagging increases the previous 581.79 cm^{-1} value. The barrier to wagging is found to be 935.76 cm^{-1} . This value is smaller than the 1110 cm^{-1} determined by Yakovlev and Godunov¹⁶ using a one-

† Supplementary material available from ref. 11. The simulated spectrum at a temperature of 2 K shows the a_1 symmetry transition $14_0^2 15_0^2$ with an intensity of 6%.

dimensional quadratic+gaussian model. The equilibrium conformation at $\theta = 186.40^\circ$, $\alpha = 39.17^\circ$ is in excellent agreement with the $\theta = 185.61^\circ$, $\alpha = 39.66^\circ$ values obtained from the MP2/6-311G(d, p) results.¹¹

Conclusions

A method has been developed for simultaneously fitting the kinetic and potential functions for several large-amplitude coordinates. The procedure minimizes the differences between the experimental and calculated energy levels using a gradient approach with explicit consideration of the hessian matrix. The application of this technique to the methyl rotation in the S_0 state of acetaldehyde shows that the use of a constant kinetic energy term has a small but appreciable effect on the barrier to rotation. The inclusion of a $\cos(9\theta)$ term in the potential function is equivalent to the introduction of a variable kinetic energy term. Both approximations reproduce the energy levels to experimental accuracy, (10^{-4} cm^{-1}) and are useful for predictive purposes. The use of models that do not include the effect of a variable kinetic constant is translated into incorrect values for the barrier to rotation as a result of the interdependence between the kinetic and potential terms.

The use of a one-dimensional model for the torsion of the methyl group in the T_1 state of acetaldehyde after refinement of the $v_{15} = 1$ and 2 experimental levels leads to a rotational barrier of 581.74 cm^{-1} . When the wagging of the carbonyl hydrogen is considered and the $v_{14} = 2$ experimental levels included, the barrier to methyl rotation increases to 633.60 cm^{-1} . Thus, it is clear that the use of one-dimensional models can lead to results affected by an appreciable margin of error when several interacting vibrations are present. The barrier to inversion in the two-dimensional case is 935.76 cm^{-1} , in contrast with the 1110 cm^{-1} value of ref. 16. The equilibrium conformation derived from the potential function yields a torsion angle of $\theta = 186.40^\circ$ and a wagging angle of $\alpha = 39.17^\circ$. These results are in very good agreement with the MP2/6-311G(d, p) values of 185.61° and 39.66° for θ and α , respectively.¹¹ These results show that the information derived from one-dimensional models and fully optimized *ab initio* results must be carefully compared to each other, as all $3N - 6$ internal coordinates are simultaneously considered in the optimization procedure.

The fitting procedure that we propose requires a good set of potential and kinetic parameters as input. These can be obtained from *ab initio* calculations. As the fitting process is responsible for the accuracy of the final function, any reasonable flexible basis set can be used. It has been shown previously that a quadratic+gaussian+cosine form for the inversion+torsion potential function requires very few selected points on the potential-energy hypersurface.^{5,11,12} With this model, both the number of energy data points generated by the *ab initio* procedures and the adjustable parameters in the expansion of the kinetic and potential energies are kept to a minimum.

References

- 1 M. A. Pariseau, I. Suzuki and J. Overend, *J. Chem. Phys.*, 1965, **42**, 2335.
- 2 T. Ueda and T. Shimanouchi, *J. Chem. Phys.*, 1967, **47**, 4042.
- 3 L. Hedberg and I. M. Mills, *J. Mol. Spectrosc.*, 1993, **160**, 117.
- 4 J. D. Lewis, T. B. Malloy, T. H. Chao and J. Laane, *J. Mol. Struct.*, 1972, **12**, 427.
- 5 C. Muñoz-Caro, A. Niño and D. C. Moule, *Chem. Phys.*, 1994, **186**, 221.
- 6 S. P. Belov, M. Yu. Tretyakov, I. Kleiner and J. T. Hougen, *J. Mol. Spectrosc.*, 1993, **160**, 61.
- 7 M. A. Harthcock and J. Laane, *J. Phys. Chem.*, 1985, **89**, 4231.
- 8 A. Niño and C. Muñoz-Caro, *Comput. Chem.*, 1994, **18**, 27.
- 9 J. D. Head and M. C. Zerner, *NATO ASI Ser., Ser. C*, 1986, **166**, 253; H. B. Schlegel, *Adv. Chem. Phys.*, 1987, **LXVII**, 249; J. D. Head, B. Weiner and M. Zerner, *Int. J. Quantum Chem.*, 1988, **XXXIII**, 177.
- 10 W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, in *Numerical Recipes in C*, Cambridge University Press, Cambridge, 1988, ch. 10.
- 11 A. Niño, C. Muñoz-Caro and D. C. Moule, *J. Phys. Chem.*, 1994, **98**, 1519.
- 12 A. Niño, C. Muñoz-Caro and D. C. Moule, *J. Mol. Struct.*, 1994, **318**, 237.
- 13 H. Gu, T. Kundu and L. Goodman, *J. Phys. Chem.*, 1993, **97**, 7194.
- 14 D. J. Clouthier and D. C. Moule, *Top. Curr. Chem.*, 1989, **150**, 167.
- 15 D. C. Moule and K. H. K. Ng, *Can. J. Chem.*, 1985, **63**, 1378.
- 16 N. N. Yakovlev and I. A. Godunov, *Can. J. Chem.*, 1992, **70**, 931.

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