J. Phys. Chem. A **2002,** *106,* 4957−4960

Interpolated Algorithm for Large-Curvature Tunneling Calculations of Transmission Coefficients for Variational Transition State Theory Calculations of Reaction Rates

Antonio Fernández-Ramos

Departamento de Química Física, Universidad de Santiago de Compostela,
Santiago de Compostela, Spain

Donald G. Truhlar

Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, Minnesota

José C. Corchado and Joaquín Espinosa-García*

Departamento de Química Física, Universidad de Extremadura, Badajoz, Spain

Received: November 14, 2001; In Final Form: February 14, 2002

We present a new algorithm for carrying out large-curvature tunneling (LCT) calculations. The new algorithm, called interpolated LCT (or ILCT) is based on interpolation by splines under tension. It is tested on five hydrogen-atom transfer reactions. We find that the cost of LCT calculations can be reduced by more than an order of magnitude.

1. Introduction

Tunneling plays a central role in the kinetics and dynamics of hydrogen atom (neutral or charged) abstraction reactions, especially at room temperature and below. The accuracy of tunneling calculations depends on the potential energy surface (PES). Furthermore, it can be limited by the availability of information about different regions of the potential energy surface. In particular, if only the stationary points are known, the very simple Wigner[1] and conservation-of-vibrational-energy Eckart[2,3] methods can be used to give a simple estimate of tunneling probabilities. When the geometries along the minimum energy path (MEP) in isoinertial coordinates, also called the intrinsic reaction coordinate (IRC)[4] or intrinsic reaction path, is available, along with a quadratic expansion of the potential in directions orthogonal to the path, the centrifugal dominant small-curvature semiclassical adiabatic ground-state (CD-SC-SAG) approximation[5,6] (in short, SCT, small curvature tunneling) gives a more accurate description of the tunneling probabilities by accounting for vibrational energy release in to and out of the reaction coordinate and for corner cutting in the limit of small reaction-path curvature.[7,8] Finally, when the PES is also known in a broader swath region on the concave side of the reaction path, it is possible to calculate the tunneling probabilities by the large-curvature tunneling (LCT) approximation,[9,10] which may be especially required for bimolecular reactions in which a light atom is transferred between two heavy atoms,[11−13] i.e., when the heavy-light-heavy mass combination is present and the reaction path transforms from the reactant Jacobi translation to the product Jacobi translation. In the LCT approximation, tunneling proceeds along straight-line paths from the entrance valley of the PES to the product valley. The LCT approximation that was widely used from 1983 until recently was the large-curvature ground-state approximation, version 3[5,14−19] (LCG3). However, it has been noted that this method sometimes overestimates the tunneling probability at low energy because of an inadequate treatment of anharmonicity.[20] Recently a new LCT approximation called LCG4, which includes a nonquadratic correction in the vibrationally nonadiabatic region of the straight tunneling paths, was proposed.[20] This approximation has already been applied to gas-phase and enzyme kinetics.[21,22]

In the LCT algorithms used so far, for each tunneling path, the energy of a certain number of points is required in order to perform numerical integration along the tunneling path. For points in the vibrationally adiabatic region near the MEP, the calculation of the energy is based on a quadratic expansion around the MEP, along which the energy and first and second derivatives with respect to all coordinates are available. However, when the tunneling path enters the nonadiabatic zone, additional energy calculations are required. Given the large number of tunneling paths needed to converge the integral over tunneling energies and the large number of points on each tunneling path required to converge the numerical integration, along the tunneling paths, the number of energy calculations in the nonadiabatic region can be significant, making the original LCT algorithm rather expensive from the computational point of view.

In this paper, we propose an interpolation method that reduces the computational cost along the tunneling paths in the large-curvature tunneling calculations by minimizing the number of points to be calculated in the nonadiabatic region of each tunneling energy. We call it the interpolated large curvature tunneling (ILCT) method in general, or ILCT-LCG4 in particular, to denote the new algorithm for treating anharmonicity. The method is tested for five hydrogen abstraction reactions.

2. Method

In LCT calculations, for each energy, a tunneling path is defined as a straight line in isoinertial coordinates between the two reaction-coordinate turning points lying on the MEP, one on the reactant side of the barrier top and one on the product side. The transmission coefficient for variational transition state theory[5,15] is then obtained by combining the probability for tunneling paths initiated by motion parallel to the reaction

---

* To whom correspondence should be addressed.

10.1021/jp014204t CCC: $22.00

coordinate and vibrational motion normal to the reaction coordinate, and these straight-line paths are used to calculate tunneling amplitudes for the latter. The transmission coefficient is then obtained from an appropriately normalized (uniformized) sum over tunneling probabilities associated with accessible final vibrational states into which tunneling occurs (in the exoergic direction of reaction) and appropriately weighted averages over the locations of the turning points that terminate the paths and over the tunneling energy, which is the total energy of the system. For a given pair of turning points and a given tunneling energy, the tunneling amplitude for a particular straight-line path is given by $T_{\mathrm{tun}} = \exp(-\theta)$, where θ is the magnitude of the imaginary part of the action integral (in atomic units) along the path. The action integral is a one-dimensional definite integral given by eq 20 of ref 5, in which the independent variable is the progress coordinate for motion along the straight-line path, and the integrand involves an effective potential. The present paper is concerned with developing an efficient way to calculate this action integral. This straight-line path is divided into three zones. Zones I and III are in the reactant and product valleys, respectively, and they are vibrationally adiabatic, and Zone II describes the middle zone of the straight-line path and is vibrationally nonadiabatic. For some PESs, region II does not exist at all energies; the limits of the nonadiabatic region are given elsewhere.[15,17,20]

In the interpolated method, ILCT, once the limits of the nonadiabatic region for each tunneling energy are found (if this region exists for that particular energy), the first step is the calculation of the "effective" potential, $\mathrm{V}^{\mathrm{II}}_{\mathrm{eff}}$, for n points in zone II of each tunneling path. In the LCT methods, this potential is given by

$$V^{\mathrm{II}}_{\mathrm{eff}}(\tilde{s}_0, \xi) = \mathrm{V}[\mathbf{x}(\tilde{s}_0, \xi)] + V^{\mathrm{I}}_{\mathrm{corr}}(\tilde{s}_0, \xi_{\mathrm{I}}) + V^{\mathrm{I}}_{\mathrm{anh}}(\tilde{s}_0, \xi_{\mathrm{I}}) + \frac{\xi - \xi_{\mathrm{I}}}{\xi_{\mathrm{III}} - \xi_{\mathrm{I}}}\{[V^{\mathrm{III}}_{\mathrm{corr}}(\tilde{s}_0, \xi_{\mathrm{III}}) - V^{\mathrm{I}}_{\mathrm{corr}}(\tilde{s}_0, \xi_{\mathrm{I}})] + [V^{\mathrm{III}}_{\mathrm{anh}}(\tilde{s}_0, \xi_{\mathrm{III}}) - V^{\mathrm{I}}_{\mathrm{anh}}(\tilde{s}_0, \xi_{|})]\}$$

where $V[\mathbf{x}(\tilde{s}_0, \xi)]$ is the classical potential to be evaluated at points ξ_i, $i = 1, ..., n$, in zone II of the straight path at a tunneling energy corresponding to the reactant-valley turning point $\tilde{s}_0$; $V^{\mathrm{I,III}}_{\mathrm{anh}}(\tilde{s}_0, \xi_{\mathrm{I,III}})$ is the LCG4 anharmonic correction to the potential, and $V^{\mathrm{I,III}}_{\mathrm{corr}}(\tilde{s}_0, \xi_{\mathrm{I,III}})$ accounts for the zero-point energy of the modes that are still within their vibrational turning points. In the original algorithm used so far, a typical value of n to get convergence is 120. In the ILCT method, the minimum number of points is $n = 3$: the two limits of the nonadiabatic region ($\xi_1 = \xi_{\mathrm{I}}$ and $\xi_3 = \xi_{\mathrm{III}}$) and a middle point ($\xi_2$). In the more general case, $n - 2$ equidistant points in isoinertial coordinates along the segment of the tunneling path that lies in the nonadiabatic zone are calculated, plus the two limit points. Thus, the minimum number of nonadiabatic energies required for the interpolated LCT calculation is three times the number of tunneling paths that have a nonadiabatic zone, which is always much lower than the cost of the original method. For higher values of n, the cost rises, but for all of the reactions tested, we always significantly reduced the cost with respect to the original algorithm. In the second step, the points $V[\mathbf{x}(\tilde{s}_0, \xi)]$ along each tunneling path are fitted to spline-under-tension[23,24] function of distance along the segment.

In the new algorithm, every time that the potential energy is needed for any point along the nonadiabatic segments of the tunneling path, this energy is calculated by means of the spline fit to the n calculated points, except in the case that the number of quadrature points in the nonadiabatic region of the tunneling path is less than the number of points (n) used to interpolation. Because the spline fitting methods of interpolation reproduce the input values, an increase of the parameter n will eventually lead to the same result as the original method. The use of spline interpolation methods allows us to obtain a continuous function, with continuous first and second derivatives, and the tension on the splines reduces the likelihood of spurious oscillations in the interpolated values. Splines also have the advantage that they are applicable for any value of n. The interpolation by splines is carried out via the generally available splines-under-tension program package TSPACK.[24]

In the previous LCT algorithm, the quadratures along each tunneling path are calculated by a single Gauss−Legendre quadrature. In the new algorithm, we retain this type of quadrature (typically with n, the number of quadrature nodes, set equal to 120), but instead of directly evaluating the potential energy function at each quadrature node, we evaluate it only at the spline nodes, and we interpolate it to the quadrature nodes. All quadratures can be carried out by Gauss−Legendre quadrature or repeated Gauss−Legendre quadrature. In the latter, the integration interval is broken into equal-length subintervals, each of which is integrated by standard Gauss−Legendre quadrature. In the present paper, we used single high-order quadrature instead of repetition, for example, a single 120-point quadrature rather than three 40-point quadratures.

Therefore, our interpolation method allows inexpensive LCT calculations whose accuracy can be increased at will by increasing the number n of points along each of the tunneling paths on the grid of tunneling paths. As n increases, the results converge to the original algorithm. The question we need to clarify is if we can obtain accurate results with low values of n, so that we can significantly reduce the cost of a LCT calculation without seriously affecting the quality of the LCT transmission probabilities.

3. Applications

We have selected five hydrogen abstraction reactions of the type A−H + B as our test set, where a hydrogen atom is transferred between two heavy atoms or groups A and B. The five reactions are described by analytical PESs: **R1**, OH + Cl with the PES by Ramachandran, Senekowitsch, and Wyatt;[25] **R2**, Br + HCl based on the PES by Kuntz, Nemth, Polanyi, Rosner, and Young;[26] **R3**, $\mathrm{CH_4}$ + O(^{3}P) based on the PES by Corchado, Espinosa-García, Roberto-Neto, Chuang, and Truhlar;[27] **R4**, $\mathrm{CH_4}$ + Cl based on the PES by Corchado, Espinosa-García, and Truhlar;[28] and **R5**, OH + $\mathrm{CH_4}$ based on the PES by Espinosa-García and Corchado.[29] The new algorithm was added to the POLYRATE program,[30] which is used for the present calculations. Note that the authors's PESs can be found on our web page, http//w3qf.unex.es/html/superficies.htm, which is freely accessible to the scientific community.

To test how well the new algorithm works, we first calculated converged tunneling probabilities using the standard number of points usually implemented ($n = 120$ for each tunneling path). Then, we performed ILCT calculations using much less data. The temperature chosen for our study was 200 K, because it is well-known that tunneling is more important at low temperature. In the ILCT calculation, we allowed the system to reach all of the accessible vibrational excited states into which tunneling proceeds. The maximum final vibrational quantum number is $n^{\mathrm{max}}_{\mathrm{p}} = 0$, 2, 1, 0, and 1 for reactions 1−5, respectively.

For a typical case, the $\mathrm{CH_4}$ + Cl reaction, Figure 1 shows the contour diagram using skewed coordinates (Jacobi type for

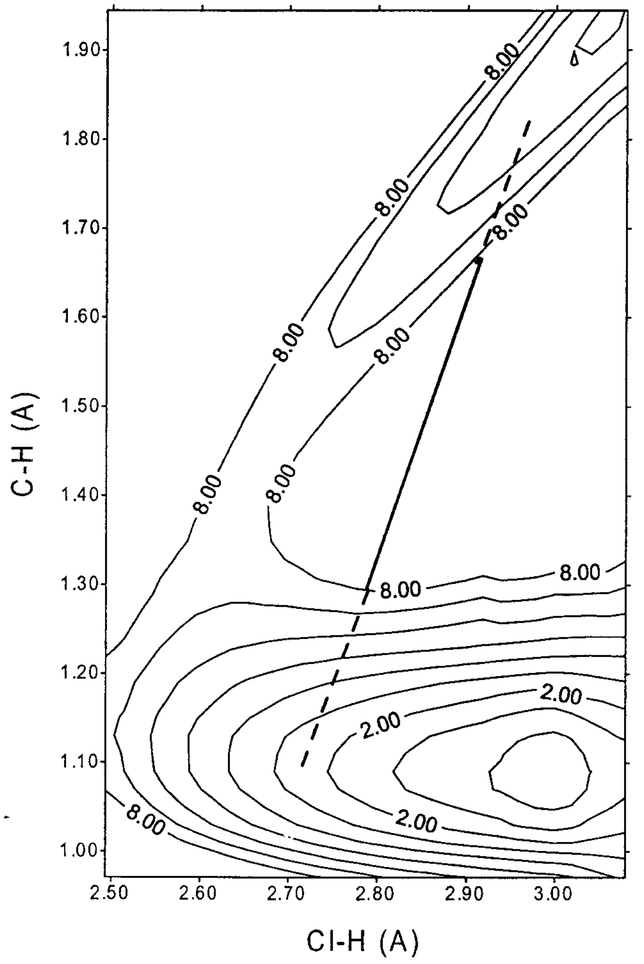

Figure 1. Contour diagram of the analytical PES for the CH_4+Cl reaction using skewed coordinates (Jacobi type) where the *Y* axis is the C−H distance and the *X* axis is the distance from the chlorine atom to the center-of-mass of the C−H bond. The contours are depicted in increments of 1 kcal mol^{-1}, and the zero of the energy is taken in the reactants. The straight line between the MEP in the reactant and product channels is the LCT tunneling path between the reaction coordinate turning points for a total energy of 29.01 kcal mol^{-1}. Dashed lines are the adiabatic zones and solid line the diabatic zone.

triatomic systems) where the *Y* axis is the C−H distance and the *X* axis is the distance from the chlorine atom to the center-of-mass of the C−H bond. On this diagram, a straight-line LCT tunneling path [adiabatic zones (dashed line) and diabatic zone (solid line)] is shown.

4. Results and Discussion

First, we test the convergence of the transmission coefficient calculated by the original algorithm with respect to the number of points along the tunneling path (Figure 2) with each tunneling energy and each final vibrational quantum number, n_p. The choice of 120 points in this study to define each tunneling path in the original algorithm is a compromise between accuracy and computational cost. For the set of five reactions studied in this paper, 200 points give a converged tunneling coefficient. With respect to this number of points, using 120 points yields an average error of only 2.9%. A reduction of the number of points for each tunneling path to 100 almost doubles the average error to 5.5%.

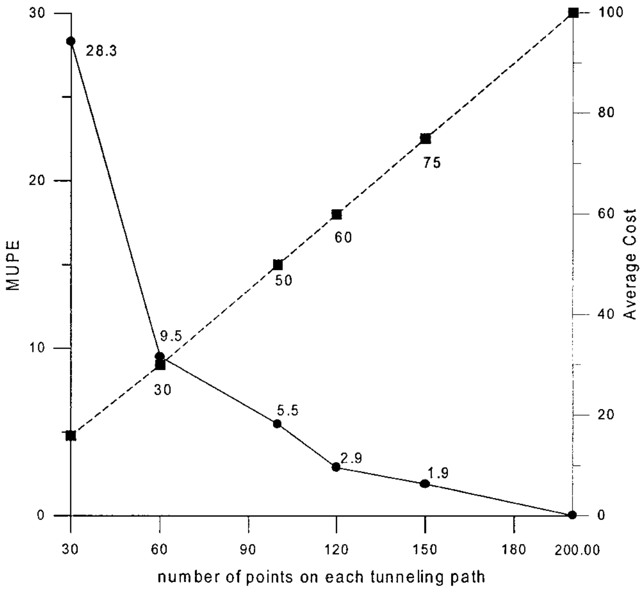

Figure 2. Mean unsigned percentage error (left axis and full line) and average percentage cost (right axis and dashed line) versus the number of quadrature points along each tunneling path in the original algorithm.

TABLE 1: Comparison of Interpolated and Benchmark Transmission Coefficients κ for Several Reactions at 200 K

		n					
reaction	benchmark[a]	11	9	7	5	4	3
Cl + OH	47.34	47.32	47.43	47.29	47.08	46.77	46.02
Br + ClH	3.10	3.10	3.10	3.10	3.10	3.10	3.13
O(^{3}P) + CH_4	69.83	71.48	70.87	68.52	61.87	44.02	26.10
Cl + CH_4	2.73	2.72	2.71	2.71	2.66	2.58	2.44
OH + CH_4	16.48	16.68	16.68	16.75	17.09	17.64	20.12
MUPE(%)[b]		0.8	0.7	0.9	3.6	10.1	19.8

[a] $n = 120$. [b] Mean unsigned percentage error with respect to the $n = 120$ benchmark calculation (which is carried out without interpolation).

TABLE 2: Number of Nonadiabatic Energies Required for Each Calculation in Table 1

		n					
reaction	benchmark[a]	11	9	7	5	4	3
Cl + OH	5255	968	846	686	505	408	306
Br + ClH	3260	737	603	476	340	272	204
O(^{3}P) + CH_4	3340	770	630	490	350	280	210
Cl + CH_4	847	220	180	140	100	80	60
OH + CH_4	3446	957	801	630	460	368	279
average cost(%)[b]	100	24	20	15	11	9	7

[a] $n = 120$. [b] Average cost with respect to the $n = 120$ converged calculation, which is 100%. For the purposes of this table, average cost is defined as average number of potential energy evaluations in the nonadiabatic zone.

Table 1 lists the transmission coefficient κ and Table 2 the total number of points in the nonadiabatic regions of the tunneling calculations (for all tunneling energies and all n_p) as a function of the number of points, *n*, used for interpolation in each nonadiabatic segment. The values in Table 2 provide an estimate of the cost in the sense that, for any but the least expensive potential energy functions, the additional cost of an LCT over the cost of an SCT one is proportional to the number of points in the nonadiabatic zone. The values without interpolation are also included as benchmark values in both tables. Note that the values in Table 2 refer to the calculation of an entire transmission coefficient, involving multiple action integrals corresponding to various turning points, final accessible vibrational states, and tunneling energies. The results of Table 1 show that when the number of points used for interpolation is very small (3 and 4 points) the average error is large (19.8 and 10.1%, respectively), but with a larger number of points (5−11), the agreement between the interpolated and noninterpolated tunneling factor is sufficiently good for quantitative dynamics calculation and provides an important computational cost saving. Thus, when this last range of n interpolated points is considered (from 5 to 11 points for each tunneling path), the maximum error in these calculations is always less than or equal to 11%. This value corresponds to the $CH_4 + O(^3P)$ reaction using only 5 interpolated points for each tunneling path. When this bad value is excluded, the maximum error is less than 4%. The results of Table 1 show that $n = 9$ is quite reliable compared to the fully converged results, and $n = 7$ is only slightly less accurate. In fact, because the benchmark $n = 120$ calculation is itself only converged to ≈3% (see above), all calculations with $n \leq 7$ are better converged with respect to the benchmark than the benchmark itself is converged. One might, therefore, use even larger numbers of Gauss−Legendre nodes in the future because increasing the number of quadrature points usually has a negligible increase in cost when the number of potential energy function evaluations (i.e., the number of spline nodes) is not increased. One could also consider using more repetitions of lower Gauss−Legendre quadratures because there is no accuracy advantage in using high-order formulas when the integrand has only two continuous derivatives.

The emphasis in the previous paragraph was on using the new method as a more efficient algorithm for fully converged calculations. However, one can also consider using it for more approximate implementations of the LCT procedure. This is especially reasonable when one considers that semiclassical methods for hydrogen tunneling tend to be accurate to only about 15% at best, and the additional physical approximations in full rate calculations employing the LCT approximation appear to have an average error closer to 25%.[31] Thus ILCT-n calculations with n even as small as three can be a reasonable choice when potential energy evaluations are expensive. Table 1 shows that ILCT-3 calculations have an average error of 20%, whereas Figure 2 shows that the original algorithm has an average error of 28% with $n = 30$ (the $n = 30$ calculations with the original algorithm were carried out with a single 30-point Gauss−Legendre quadrature).

We note two possible directions for further improvements. First, note that in the present implementation the selected points in the nonadiabatic region of the tunneling path are equidistant. A more complicated alternative would be an adaptative algorithm, for example, one could first calculate these evenly spaced points and then use these results to guide where to put the next two points, and so forth. Second, one could consider a two-dimensional interpolation in which the potential energy function is interpolated not only as a function of ξ for a given tunneling energy and a given final vibrational quantum number n_p but also as a function of tunneling energy (or, equivalently, as a function of the reaction-coordinate turning point[5] $\tilde{s}_0$). In the latter case, one would interpolate as a function of ξ and $\tilde{s}_0$ for each final vibrational quantum number n_p.

5. Concluding Remarks

We have presented and tested an interpolation scheme for carrying out large-curvature tunneling calculations. For a test suite of five reactions, the mean unsigned percentage error (MUPE) for each interpolated number of points is (in %): 3.6, 0.9, 0.7, and 0.8 for 5, 7, 9, and 11 interpolated points, respectively, whereas the computational cost with respect to the benchmark calculation (100%) is reduced from 24 to 11% when the interpolated number of points pass from 11 to 5 (Table 2).

The new interpolated algorithm, in conjuntion with direct dynamics, will provide a promising tool for the calculation of transmission coefficients in large systems with the heavy−light−heavy mass combination, for which the original algorithm based on the calculation of the potential energy function at each quadrature node is very expensive.

Acknowledgment. This work is supported in part by Consejeria de Educación, Ciencia y Tecnología, Junta de Extremadura, Spain (Projects No. IPR99A009 and 2PR01A002) and by the U.S. Department of Energy, Office of Basic Energy Sciences. A.F.R. thanks Ministerio de Ciencia y Tecnología (Spain) for a “Ramón y Cajal” research contract.

References and Notes

(1) Wigner, E. *Z. Phys. Chem. Abt. B* **1932**, *19*, 203.
(2) Eckart, C. *Phys. Rev.* **1930**, *35*, 1303.
(3) Truhlar, D. G.; Kuppermann, A. *J. Am. Chem. Soc.* **1971**, *93*, 1840.
(4) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.
(5) Lu, D.-h.; Truong, T. N.; Melissas, V. S.; Lynch, G. C.; Liu, Y.-P.; Garrett, B. C.; Steckler, R.; Isaacson, A. D.; Rai, S. N.; Hancock, G. C.; Lauderdale, J. G.; Joseph, T.; Truhlar, D. G. *Comput. Phys. Commun.* **1992**, *71*, 235.
(6) Liu, Y.-P.; Lynch, G. C.; Truong, T. N.; Lu, D−h.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc.* **1993**, *115*, 2408.
(7) Marcus, R. A.; Coltrin, M. E. *J. Chem. Phys.* **1977**, *67*, 2609.
(8) Skodje, R. T.; Truhlar, D. G.; Garrett, B. C. *J. Chem. Phys.* **1982**, *77*, 5955.
(9) Garrett, B. C.; Truhlar, D. G.; Wagner, A. F.; Dunning, T. H., Jr. *J. Chem. Phys.* **1983**, *78*, 4400.
(10) Bondi, D. K.; Connor, J. N. L.; Garrett, B. C.; Truhlar, D. G. *J. Chem. Phys.* **1983**, *78*, 5981.
(11) Babamov, V. K.; Marcus, R. A. *J. Chem. Phys.* **1978**, *74*, 1790.
(12) Kreevoy, M. M.; Ostovi, D.; Truhlar, D. G.; Garrett, B. C. *J. Phys. Chem.* **1986**, *90*, 3766.
(13) Truhlar, D. G. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1740.
(14) Garrett, B. C.; Truhlar, D. G. *J. Chem. Phys.* **1983**, *79*, 4931.
(15) Truhlar, D. G.; Isaacson, A. D.; Garrett, B. C. In *Theory of Chemical Reactions*; Baer, M., Ed.; CRC: Boca Raton, FL, 1985; Vol. 4, pp 65−137.
(16) Garrett, B. C.; Abusalbi, N.; Kouri, D. J.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *83*, 2252.
(17) Garrett, B. C.; Joseph, T.; Truong, T. N.; Truhlar, D. G. *Chem. Phys.* **1989**, *136*, 271.
(18) Truong, T. N.; Lu, D.-h.; Lynch, G. C.; Liu, Y.-P.; Melissas, V.; Stewart, J. J. P.; Steckler, R.; Garrett, B. C.; Isaacson, A. D.; González-Lafont, A.; Rai, S. N.; Hancock, G. C.; Joseph, T.; Truhlar, D. G. *Comput. Phys. Commun.* **1993**, *75*, 143.
(19) Liu, Y.-P.; Lu, D.-h.; González-Lafont, A.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc.* **1993**, *115*, 7806.
(20) Fernández-Ramos, A.; Truhlar, D. G. *J. Chem. Phys.* **2001**, *114*, 1491.
(21) Albu, T.; Corchado, J. C.; Truhlar, D. G. *J. Phys. Chem. A* **2001**, *105*, 8465.
(22) Alhambra, C.; Corchado, J.; Sánchez, M. L.; Garcia-Viloca, M.; Gao, J.; Truhlar, D. G. *J. Phys. Chem. B* in press.
(23) Renka, R. J. *J. Stat. Comput.* **1987**, *8*, 393.
(24) Renka, R. J. *Trans. Math. Software* **1993**, *19*, 81.
(25) Ramachandran, B.; Senekowitsch, J.; Wyatt, R. E. *J. Mol. Struct. (THEOCHEM)* **1996**, *338*, 57.
(26) Kuntz, P. J.; Nemth, E. M.; Polanyi, J. C.; Rosner, S. D.; Young, C. E. *J. Chem. Phys.* **1966**, *44*, 1168.
(27) Corchado, J. C.; Espinosa-García, J.; Roberto-Neto, O.; Chuang, Y.-Y.; Truhlar, D. G. *J. Phys. Chem.* **1998**, *102*, 4899.
(28) Corchado, J. C.; Espinosa-García, J.; Truhlar, D. G. *J. Chem. Phys.* **2000**, *112*, 9375.
(29) Espinosa-García, J.; Corchado, J. C. *J. Chem. Phys.* **2000**, *112*, 5731.
(30) Corchado, J. C.; Chuang, Y.-Y.; Fast, P. L.; Villà, J.; Hu, W.-P.; Liu, Y.-P.; Lynch, G. C.; Nguyen, K. A.; Jackels, C. F.; Melissas, V. S.; Lynch, B. J.; Rossi, I.; Coitiño, E. L.; Fernández-Ramos, A.; Steckler, R.; Garrett, B. C.; Isaacson, A. D.; Truhlar, D. G. POLYRATE, version 8.5: University of Minnesota, Minneapolis, MN, 2000.
(31) Allison, T. C.; Truhlar, D. G. In *Modern Methods for Multidimensional Dynamics Computations in Chemistry*; Thompson, D. L., Ed.; World Scientific: Singapore, **1998**; pp 618−712.