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Combining Quantum Mechanical Calculations And A χ^2 Fit In A Potential Energy Function For The $\text{CO}_2 + \text{O}^+$ Reaction

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In order to compute a highly accurate statistical rate constant for the $\text{CO}_2 + \text{O}^+$ reaction, it is necessary to first calculate the potential energy of the system at many different geometric configurations. Quantum mechanical calculations are very time-consuming, making it difficult to obtain a sufficient number to allow for accurate interpolation. The number of quantum mechanical calculations required can be significantly reduced by using known relations in classical physics to calculate energy for configurations where the oxygen is relatively far from the CO_2 . A chi-squared fit to quantum mechanical points is obtained for these configurations, and the resulting parameters are used to generate an equation for the potential energy. This equation, combined with an interpolated set of quantum mechanical points to give the potential energy for configurations where the molecules are closer together, allows all configurations to be calculated accurately and efficiently.

Key words: Potential energy surface, χ^2 fit

Introduction

The reaction of carbon dioxide with the O^+ oxygen ion is of interest because experimental rate measurements show that at low energies the rate is constant at the expected value, but at high energies the rate steadily decreases to values below the expected rate (Viggiano, et al., 1992). RRKM rate calculations were done for the purpose of explaining this experimentally observed decrease (Forst, 1973).

In order to calculate the rate of reaction using statistical rate theories such as RRKM theory, the potential energy of the reacting molecules must be known at any geometric configuration that might be found near the transition state. This refers to the small portion of the potential surface that is near the maximum point on the minimum-energy path.

The accuracy of a rate calculation is directly related to the accuracy of the potential surface employed, and a good potential is needed if the rate calculation is to be highly accurate. Because calculating the potential energy at any one configuration involves time-consuming quantum mechanical calculations, constructing the potential surface with energies for all probable configurations near the transition state using quantum mechanical calculations becomes an impossible task. Instead, it is common to do calculations at judiciously chosen configurations and use interpolation to obtain good approximations for the energies of configurations for all other geometries.

The potential is split into long and short-range portions in order to further reduce the number of quantum mechanical calculations. *Ab initio* quantum mechanical calculations were done for the short-range portion only. At separation distances of 6.9 Å or greater, the long-range portion of the potential is invoked. It consists of a fit to the long range *ab initio* points with a functional form, which is a parameterized variation of the ion-induced dipole plus quadrupole potential:

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$$V = -\frac{q^2\alpha}{2r^4} + \frac{Q}{2} \frac{[(3\cos^2\theta) - 1]}{r^3} \quad (1)$$

where r is the distance between the ion and the carbon in the CO_2 , θ is the angle formed by the CO_2 axis and the line connecting the ion and the carbon atom in the CO_2 , and Q is the quadrupole moment.

Methodology

Quantum Mechanical Calculations

The short-range portion of the potential is calculated with the Gaussian 86 suite of programs (Frisch, et al., 1984). MP2 calculations are done using a 6-311++G** basis set. The r and θ values shown in Figure 1 below are varied appropriately. At separation distances (r 's in Fig. 1) of 1.9 to 6.9 Å, the short-range portion of the potential is a grid of points with spacings every 15° and 0.4 Å connected by a spline fit. Extra data points were added at $r = 2.3$ Å and 2.1 Å and $\theta = 90^\circ$, 105° , 120° , and 135° and at $r = 1.9$ Å and $\theta = 90^\circ$. The potential energies between the grid points were obtained by means of a cubic spline interpolation (Press, et. al, 1992). These energies are given in Table 1.

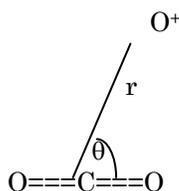


Fig. 1. Parameters used to describe potential surface

Long Range Potential

Because quantum chemistry calculations are time-consuming, it is generally more efficient to use classical physics to calculate the potential whenever accuracy allows it. Classical physics gives long-range potential energy terms, which are exact at large separation distances and provide a good analytic form for the long range potential as long as the separation distance is large.

The two potentials which need to be evaluated are the potential which the O^+ ion induces in the CO_2 and that which is produced by

the CO_2 's charge distribution. The sum of these two potentials provides the analytic form which contains parameters fit to *ab initio* data by minimizing the χ^2 function:

Table 1. MP2/6-311++G** Energies (cm^{-1})

	90°	105°	120°	135°	150°	165°	180°
1.9 Å	3295	-	-	-	-	-	-
2.1 Å	1659	471	492	11363	-	-	-
2.3 Å	1023	-463	-2744	354	-	-	-
2.5 Å	776	-438	-3224	-4121	2833	19351	30093
2.9 Å	627	-89	-2087	-4550	-5457	-3461	-1698
3.3 Å	565	115	-1163	-2981	-4644	-5363	-5391
3.7 Å	496	194	-663	-1899	-3710	-4048	-4332
4.1 Å	421	208	-388	-1251	-2156	-2825	-3067
4.5 Å	349	195	-236	-856	-1511	-2005	-2187
4.9 Å	286	172	-148	-609	-1095	-1465	-1604
5.3 Å	236	150	-94	-447	-818	-1101	-1208
5.7 Å	199	131	-60	-335	-625	-846	-929
6.1 Å	170	115	-38	-258	-487	-662	-727
6.5 Å	147	102	-24	-203	-387	-527	-579
6.9 Å	128	90	-19	-162	-313	-427	-469

$$\chi^2 = \sum_n \left| \frac{V_{\text{fit}} - V_{\text{abinitio}}}{V_{\text{abinitio}}} \right|^2 \quad (2)$$

where n is the number of points used for the fit, V_{fit} is the value of the fitted potential at each point, and the V_{abinitio} are the *ab initio* data points used in the fitting process (Bevington & Robinson, 1992). The parameters, which are fit to the *ab initio* points, are the isotropic polarizabilities and the quadrupole moments of CO_2 . The fit uses the *ab initio* values obtained from Hartree-Fock calculations to begin the parameter search (Levine, 1991). This long-range potential is used to describe the $\text{CO}_2 + \text{O}^+$ system at separation distances larger than 6.9 Å.

The Ion-Induced Dipole Term of the Long Range Potential

The ion-induced dipole potential,

$$V(r) = -\frac{q^2 \alpha}{2r^4} \quad (3)$$

where q is the charge on the ion, α is the polarizability of the neutral, and r is the distance between the ion and the center of mass of the neutral, is the potential which the O^+ induces in the CO_2 (Gilbert & Smith, 1990). The polarizability may be expressed as a second order perturbation correction to the dipole moment (Levine, 1991) in a Taylor series expansion of the classical energy of a molecule in the presence of an electric field (Flyglare, 1978).

$$W = W^o + \sum_{\alpha} E_{\alpha} \left(\frac{\partial W}{\partial E_{\alpha}} \right)_{E_{\alpha}=0} + \frac{1}{2} \sum_{\alpha, \beta} E_{\alpha} E_{\beta} \left(\frac{\partial^2 W}{\partial E_{\alpha} \partial E_{\beta}} \right)_{E_{\alpha}=0, E_{\beta}=0} + \dots \quad (4)$$

where W is the classical potential energy due to the electric field, \mathbf{E} , and α and β are the indices for the coordinates. $\left(\frac{\partial W}{\partial E_{\alpha}} \right)_{E_{\alpha}=0}$ in the first term of

equation 4 is the dipole moment of the molecule and $\left(\frac{\partial^2 W}{\partial E_{\alpha} \partial E_{\beta}} \right)_{E_{\alpha}=0, E_{\beta}=0}$ in the second term

is the polarizability tensor. In the case of the CO_2 molecule, the dipole moment is zero and the off diagonal elements of the polarizability tensor are zero, reducing equation 4 to the simpler form:

$$W = W^o - \frac{1}{2} \sum_{i=1}^3 \alpha_{ii} E_i^2 \quad (5)$$

The minus sign in Equation 5 is added in order to keep the sign of the polarizability tensor consistent with convention. Because the energy given in Equation 5 is generated from the O^+ point charge, the electric field, \vec{E} , is given by:

$$\vec{E} = \frac{q}{r^2} \quad (6)$$

where q is the charge on the ion and r is the distance between the center of mass of the CO_2 molecule and the O^+ ion. The electric field vector points along the same direction as the vector connecting the center of mass of the CO_2 molecule and the O^+ ion. With θ the same angle as shown in the picture in Figure 1, the angle between the line connecting the CO_2 center of mass and the O^+ ion and the line along the body of the CO_2 molecule, the components of the electric field vector areas follows, for a system lying in the x - z plane:

$$E_x = \frac{q}{r^2} \sin \vartheta \quad (7)$$

$$E_z = \frac{q}{r^2} \cos \vartheta \quad (8)$$

and the second derivative term in (5) becomes:

$$W^{(2)} = -\frac{1}{2} \frac{q^2}{r^4} \left(\alpha_{xx} \sin^2 \vartheta + \alpha_{zz} \cos^2 \vartheta \right) \quad (9)$$

Comparing Equation 9 with Equation 3, it is clear that $\left(\alpha_{xx} \sin^2 \vartheta + \alpha_{zz} \cos^2 \vartheta \right)$ is the anisotropic form of the polarizability, α in Equation 3. Equation 9 is the form of the ion-induced dipole potential used in the program that fits the anisotropic polarizabilities to the *ab initio* data. The initial values in the fitting program are the quantum mechanical ones generated from MP2/6-311⁺⁺G** calculations shown in Table 2.

In carrying out the fit, it is important to use the anisotropic form of the polarizability since otherwise all of the angular dependence of the long range potential is in the quadrupole term, giving it a physically unrealistic value, and possibly affecting the accuracy of the potential.

Table 2. Parameters for the Long Range Potential

	<i>Ab initio</i>	Fitted
α_{xx} (\AA^3)	1.85	1.68
α_{zz} (\AA^3)	3.24	3.68
Θ_{xx} (Debye- \AA)	-12.12	-11.89
Θ_{zz} (Debye- \AA)	-15.95	-16.53

Note: *ab initio* calculations are done at the MP2/6-311⁺⁺G** level

Quadrupole Term of the Long Range Potential

The other term of the long range potential is derived from the potential generated by the CO₂ molecule. The potential generated by a collection of charges, q_α , at a point outside of the body of charges can be expressed as a Taylor series expansion

$$\Phi = \sum_{\alpha} \frac{q_{\alpha}}{r} + \sum_{\alpha,i} q_{\alpha} x_{\alpha,i} \frac{\partial}{\partial x_i} \left(\frac{1}{r} \right) + \frac{1}{2} q_{\alpha} \sum_{i,j} x_{\alpha,i} x_{\alpha,j} \frac{\partial^2}{\partial x_i \partial x_j} \left(\frac{1}{r} \right) + \dots \quad (10)$$

where r is the distance between the origin and the point and $x_{\alpha,i}$ is the distance between the origin and the charge q_{α} (Marion & Heald, 1980). The first term is the monopole term, the second is the dipole term, and the third is the quadrupole term. Although there are several ways to express the quadrupole moment, all of them are based on this third term, which can also be expressed in the form:

$$\Phi^{(3)} = \frac{1}{6} \sum_{i,j} Q_{ij} \frac{(3 x_i x_j - r^2 \delta_{ij})}{r^5} \quad (11)$$

where the Q_{ij} are components of the quadrupole tensor, r is the distance from the center of mass of the CO₂ molecule to the ion, and the x_i are the components of the vector, \mathbf{r} . This definition of the quadrupole moment is called a traceless quadrupole moment because the trace, $\sum_i Q_{ii} = 0$. If the axis along the body of the CO₂ molecule is defined as the z -axis, and the carbon atom is at the origin, the off-diagonal elements of the quadrupole tensor are zero and $Q_{xx} = Q_{yy}$. Because the trace is zero, $Q_{zz} = -2Q_{xx}$ and there is only one independent element in the quadrupole tensor. Equation 11 becomes:

$$\begin{aligned} \Phi^{(3)} &= \frac{Q_{zz}}{6r^5} \left(-\frac{3}{2}x^2 - \frac{3}{2}y^2 + 3z^2 \right) \\ &= -\frac{Q_{zz}}{4r^5} (r^2 - 3z^2) = \frac{Q_{zz}}{4r^3} (3 \cos^2 \theta - 1) \end{aligned} \quad (12)$$

where θ is the angle formed by the line connecting the carbon in CO₂ and the oxygen ion and the z -axis. The third portion of Equation 12 is the form used for the potential generated by the CO₂ molecule at the location of the oxygen ion.

Quantum mechanical parameters were used instead of experimental ones in the long range potential because (a) a smooth and continuous transition is needed to the short range quantum mechanical potential, and (b) a good comparison between the two is needed in order to decide at what separation distance to change from the long to short range potential. The quantum mechanical quadrupole moments which come out of Gaussian 86 are not the traceless Q 's in Equation 12, but instead correspond to another definition (Hirschfelder, et al., 1954):

$$\Theta_{ij} = \sum_{\alpha} q_{\alpha} x_{\alpha,i} x_{\alpha,j} \quad (13)$$

where q_i are the individual charges and $x_{\alpha,i}$ is the i component of the vector, \mathbf{r} , connecting the charge α to the origin. The analogous traceless definition is (Marion & Heald, 1980):

$$Q_{ij} = \sum_{\alpha} q_{\alpha} (3 x_{\alpha,i} x_{\alpha,j} - r_{\alpha}^2 \delta_{ij}) \quad (14)$$

Substituting equation.13 into 14,

$$Q_{zz} = 3\Theta_{zz} - (\Theta_{xx} + \Theta_{yy} + \Theta_{zz}) \quad (15)$$

and because for the CO₂ molecule, $\Theta_{xx} = \Theta_{yy}$,

$$Q_{zz} = 2(\Theta_{zz} - \Theta_{xx}) \quad (16)$$

hence, Equation 12 becomes:

$$\Phi^{(3)} = \frac{(\Theta_{zz} - \Theta_{xx})}{2r^3} (3 \cos^2 \theta - 1) \quad (17)$$

The potential energy due to the electric field generated by the CO₂ molecule at a point located a distance r from the carbon is:

$$V = q \frac{(\Theta_{zz} - \Theta_{xx})}{2r^3} (3 \cos^2 \theta - 1) \quad (18)$$

where q is the charge on the O^+ ion. Equation 18 is the form used in the fitting program and the values for the quadrupole moments, Θ_{zz} and Θ_{xx} , are generated by Gaussian 86 and given in Table 2.

Results

Combination of Terms to Form the Long-Range Potential

Equations 9 and 18 are added together to give the final form for the long range potential. The two anisotropic polarizability parameters and the two quadrupole moment ones are optimized by doing the χ^2 fit (Equation 2) to MP2/6-311++G** data points with separation distances of 6.9 Å to 18 Å. Figure 2 shows how the long range potential using the optimized values obtained from the χ^2 fit compares to the *ab initio* points. The long-range form gives a very accurate representation of the quantum mechanical potential at separation distances larger than 6.9 Å. For this reason, the quantum mechanical grid of points was calculated only for separation distances less than 6.9 Å, and the ion-induced dipole plus quadrupole long range potential was used at larger separation distances. Figure 3 is a contour plot of the entire potential surface.

Conclusion

It has been demonstrated that a substantial reduction in the amount of time required to produce an accurate potential surface may be obtained by combining the short-range quantum mechanical portion with the less-time intensive long-range one. Starting with an appropriate functional form, the ion-induced dipole and the quadrupole potentials of classical physics, the long-range potential was generated by doing a χ^2 fit of four parameters to the highly accurate *ab initio* quantum mechanical points. The fitted form of the potential provides the accuracy needed without resorting to difficult quantum mechanical calculations.

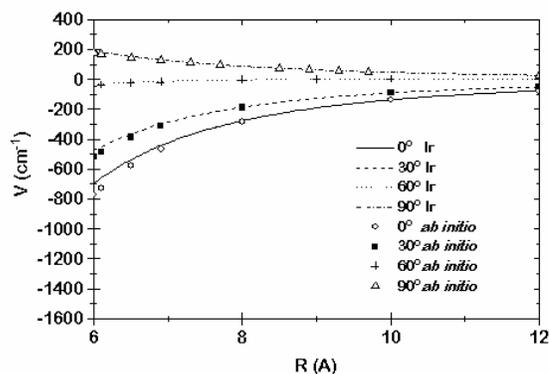


Fig. 2. Comparison of the long range potential with optimized parameters to *ab initio* points.

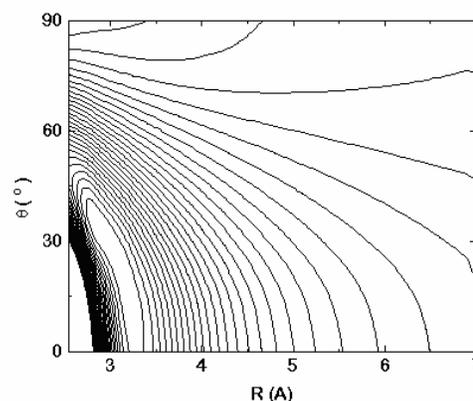


Fig. 3. Contour plot of the complete potential surface for the $CO_2 + O^+$ system. The contour at the top left corner is 548 cm^{-1} and that in the bottom of the well is -5328 cm^{-1} . The contours are spaced 226 cm^{-1} apart.

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