Theoretical Studies of Collisional Relaxation of Highly Excited SO₂ in an Ar Bath

György Lendvay

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P.O.Box 17, Hungary

George C. Schatz

Department of Chemistry, Northwestern University, Evanston, IL 60208-3113 USA

Lawrence B. Harding

Theoretical Chemistry Group, Chemistry Division, Argonne National Laboratory, Argonne IL 60439 USA

¹ Also, Visiting Scientist, Argonne National Laboratory.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
Abstract

This paper describes molecular dynamics studies of collisional relaxation of highly excited SO$_2$ in an Ar bath. Most of the calculations use a newly developed global \textit{ab initio} potential surface for SO$_2$ that correctly describes the superoxide (SOO) and ring isomers of SO$_2$ that occur as secondary minima on the ground state potential surface at high energies (about 75\% of the dissociation energy) above the C$_{av}$ minimum. Rate constants for the S + O$_2$ and O + SO reactions are calculated to test this surface, and to examine the importance of electronically excited states in the O + SO recombination. The Ar + SO$_2$ collisions are described by summing the \textit{ab initio} potential with empirical intermolecular potentials. The resulting average vibrational energy transfer $\langle \Delta E \rangle$ per collision is in good agreement with direct measurements (done at energies where the secondary minima are not populated) at 1000K, but the agreement is poorer at 300K. The agreement is significantly better than was obtained in a previous theoretical study, and our results indicate that the use of improved intramolecular and intermolecular potentials is crucial to obtaining the better results. The energy dependence of $\langle \Delta E \rangle$ is found to be much stronger at energies where the secondary minima on the potential surface are accessible, however much of this effect is reproduced using a potential that has the same dissociation energy but not the secondary minima.
I. Introduction

Collisional relaxation of highly vibrationally excited SO₂ in a thermal bath is one of the better characterized "small" polyatomic molecule relaxation problems. In fact, SO₂ is unique among small molecules in that its relaxation has been studied both by direct methods¹, in which energy in the excited molecule is determined as a function of time after initial excitation by photoabsorption, and by indirect methods², in which the competition between relaxation and SO₂ dissociation to O + SO is used in modelling O + SO recombination to infer the energy transfer rate. SO₂ is also somewhat special in that there is strong evidence in the O + SO recombination experiments² that excited electronic states of SO₂ participate actively in the kinetics. This leads to uncertainty in the comparison of direct and indirect values of <ΔE>, as the direct values are measured at energies well below dissociation where only one potential surface is significant, while the indirect measurements refer to energies close to the dissociation energy where several surfaces can be populated. However, Heymann et al¹⁴ were able to obtain good agreement between the direct and indirect values of <ΔE> for SO₂ relaxation in an Ar bath by: (1) extrapolating the direct value of <ΔE> to the dissociation energy by assuming that the energy dependence of <ΔE> retains its low energy quadratic form all the way to dissociation, and (2) determining the indirect <ΔE> values from the measured collisional efficiency factor βc for an Ar bath relative to a C₃F₈ bath, where C₃F₈ is assumed to be a strong collider. The relationship between <ΔE> and βc was taken from the exponential model³ of the energy transfer probability function. The good agreement between the direct and indirect energy transfer results suggests that the two assumptions above are valid. However, a consistency check in which classical molecular dynamics methods were used to calculate <ΔE>⁴ gave results that are in poor
agreement with the direct measurements, with the calculated $<\Delta E>$'s being much too high.

In this paper we reexamine $\mathrm{SO}_2$ relaxation by $\mathrm{Ar}$ using theory with a new potential surface for the $\mathrm{SO}_2$ molecule, a better intermolecular potential, and improved theoretical molecular dynamics methods. The primary goals of this work are: (1) to determine the nature of the comparison between calculated and measured $<\Delta E>$'s based on direct measurements, (2) to study the energy dependence of $<\Delta E>$ from low energy to the dissociation threshold to see how to do the extrapolation that is needed to interrelate the direct and indirect experiments. In addition, we will determine the importance of the superoxide (SOO) and cyclic ring $\mathrm{SO}_2$ minima on the energy dependence of $<\Delta E>$, we will reexamine the role of excited electronic states in the $\mathrm{O} + \mathrm{SO}$ recombination, and we will study the functional form of the energy probability distribution function to see if the previously assumed exponential distribution function is reasonable.

To calculate $<\Delta E>$, we use classical molecular dynamics methods that we have previously used in extensive studies of energy transfer from highly excited $\mathrm{CS}_2$ and $\mathrm{SF}_6$.\textsuperscript{5,6,7,8} The $\mathrm{CS}_2$ studies are especially relevant here, as Hippler, Troe and coworkers\textsuperscript{19} have used the same experimental method to study both $\mathrm{CS}_2$ and $\mathrm{SO}_2$ relaxation at comparable energies, and with the same bath gases. Our calculated $<\Delta E>$'s for $\mathrm{CS}_2$ relaxation with rare gas collision partners are generally within a factor of two of experiment, which is about the best that one can expect given the uncertainty in the calculated results because the potentials are not well known, and because of possible errors in the experiments arising from the calibration process used to define the energy content of the molecule. There are also potential problems in the calculated results due to quantum effects (whose magnitude is not known), and from incomplete intramolecular vibrational
redistribution (IVR). Our approach assumes that IVR is rapid compared to the time between collisions, which is probably reasonable at high energies close to dissociation but not at low energies where vibrational motion is regular. Other assumptions are possible (such as neglecting IVR between collisions\textsuperscript{10}), however we have found that the rapid IVR assumption gives the best comparisons with experiment even at relatively low energies.

The theoretical studies by Hippler et al\textsuperscript{4} of SO\textsubscript{2} relaxation used molecular dynamics methods that are similar to what we use here, but with several differences in implementation. They developed an intramolecular potential for SO\textsubscript{2} that is given by a sum of three Morse functions, with the parameters adjusted so that the SO\textsubscript{2} geometry and dissociation energy are correct, and the vibrational frequencies are roughly correct. The intermolecular potential was written as a sum of three identical Lennard-Jones pair potentials. Several choices of parameters for these potentials were considered, including one (the LLJ potential) that probably overestimates the range of the potential, and another (the SLJ potential) that underestimates it. Other differences between our calculations and those of Hippler et al refer to the choice of maximum impact parameter \( b_{\text{max}} \), and in details of the sampling of initial rotational energy.

The significance of electronically excited states in O + SO recombination was studied in detail by Cobos et al\textsuperscript{2}. They found that the high pressure limit rate constant was about twice the maximum possible value that they could obtain from the statistical adiabatic channel model for a single reactive potential. Similarly, the low pressure rate constant implied a (single surface) collisional efficiency factor \( \beta_c \) of 3.0 for Ar, and 25.2 for C\textsubscript{2}F\textsubscript{6}, which is clearly unphysical. They used estimated properties of the known stable excited states of SO\textsubscript{2} to estimate the contribution of these states to the results, and they concluded that the high and low pressure limit
results are roughly an order of magnitude higher than what they would have been for the ground surface alone. There is a lot of uncertainty in these results, which is the primary reason why only the relative $\beta_e$ values were used to compare with the direct measurements.

To summarize the rest of the manuscript, in the next section we describe the new SO$_2$ surface, along with tests of the surface that include the calculation of rate constants for S + O$_2$ and O + SO. Section III presents details of the Ar + SO$_2$ energy transfer calculations and the comparison with experiments and previous theory. Section IV summarizes our conclusions.

II. SO$_2$ Potential Energy Surface

A. Ab Initio Calculations and Surface Fitting

  Ab initio electronic structure calculations have been used to characterize global features of the SO$_2$ potential surface including the global minimum (OSO), the ring isomer, the superoxide isomer (SOO), and the O+SO and S+O$_2$ asymptotes. To represent the potential surface, we have used a many-body decomposition in which different quality calculations are used to determine the two and three body terms.

  In the many-body decomposition, the potential energy is expressed as:

  \[ V_{\text{tot}} = V_2(R_1, R_2, R_3) + V_3(R_1, R_2, R_3) \]

  where,

  \[ R_1 = R(S-O) \]

  \[ R_2 = R(S-O) \]

  \[ R_3 = R(O-O) \]
and the two-body potential $V_2$ is given by:

$$V_2(R_1,R_2,R_3) = V_{so}(R_1) + V_{so}(R_2) + V_{oo}(R_3).$$

Characterization of the terms that make up $V_2$ involves mapping out only two one-dimensional, diatomic, potential curves and hence requires calculations at only a small number of geometries. Characterization of the three-body potential, $V_3$, involves calculations over a three-dimensional grid of geometries and hence requires a large number of calculations. As a compromise between the accuracy of the final surface and the computational expense we have evaluated the two-body potential at a relatively high level of theory and the three-body potential at a much lower level. The details of this procedure are summarized below. All calculations were carried out on an Alliant, FX-2800 computer using the COLUMBUS package of codes\textsuperscript{12}. (1) $V_{oo}$

The ab initio calculations on $O_2$ are multi-reference, singles and doubles configuration interaction, CI, calculations from a full-valence complete active space, CASSCF, reference wavefunction. These calculations were done with two basis sets, these being the Dunning\textsuperscript{13}, correlation-consistent, polarized valence double zeta and polarized valence triple zeta bases. With the triple zeta basis set the calculated dissociation energy is in error by 4.6 kcal mol\textsuperscript{-1} (calculated $D_0=113.0$ kcal mol\textsuperscript{-1}, experimental $D_0=118.1$ kcal mol\textsuperscript{-1}). To correct this we define an error function to be the difference between the double zeta and triple zeta potential curves. The final $V_{oo}$ is then defined to be the triple zeta potential plus a constant times the error function, with the constant chosen such that $V_{oo}$ reproduces the known bond energy of $O_2$. The functional form used to fit $V_{oo}$ is a one-dimensional, cubic spline. The spectroscopic constants from the adjusted potential are in good agreement with experiment, (calculated $\omega_e = 1564$ cm\textsuperscript{-1}, experimental $\omega_e =
1580 cm$^{-1}$, calculated $\omega_x = 10.4$ cm$^{-1}$, experimental $\omega_x = 12.0$ cm$^{-1}$).

(2) $V_{so}$

The calculations on SO differ from those on OO in that it was only possible to carry out the CI calculations with a polarized valence double-zeta basis set. At this level, the calculated SO bond energy is in error by 29 kcal mol$^{-1}$. To correct this, the error function defined above was first scaled by the ratio of the equilibrium bond lengths, i.e.,

$$E_{so}[R] = E_{oo}[R^*(R_o(00)/R_o(SO))]$$

The final $V_{so}$ is then defined to be the double zeta potential curve plus a constant times the scaled error function with the constant chosen such that $V_{so}$ reproduces the known bond energy of SO (123.6 kcal mol$^{-1}$). The spectroscopic constants on the resulting adjusted potential curve are in reasonable agreement with experiment, (calculated $\omega_o = 1055$ cm$^{-1}$, experimental $\omega_o = 1148$ cm$^{-1}$, calculated $\omega_x = 3.6$ cm$^{-1}$, experimental $\omega_x = 6.1$ cm$^{-1}$).

(3) $V_3$

The three-body potential was calculated using a 12 electron - 9 orbital CASSCF wavefunction with Dunning’s correlation consistent, polarized double zeta basis set.$^{13}$ The active orbitals in this calculation consist of all nine valence $p$ orbitals, three on each center. Allowing 12 electrons to occupy the 9 active orbitals in all possible ways leads to 1292 configurations. While a CASSCF calculation of this size is quite tractable, the inclusion of dynamic correlation effects via a singles and doubles configuration interaction calculation from this reference (2,725,178 configurations) would be feasible only at a small number of geometries. For this reason the three-body potential was evaluated at the CASSCF level without the inclusion of higher order CI effects. It should be noted that the neglected dynamic correlation has a profound
effect on the potential surface. For example, at the CASSCF level the bond energy of SO$_2$ is only 77 kcal mol$^{-1}$, to be compared to an experimental result of 130 kcal mol$^{-1}$. As will be described below, inclusion of dynamic correlation effects in the two-body potential alone largely corrects this error.

The CASSCF calculations were carried out over a three dimensional grid of points in each of two coordinate systems. In each coordinate system the three coordinates are $R_{AB}$, $R_C$, $\theta_C$, where A, B and C are S, $O_a$ or $O_b$. $R_C$ is defined to be the distance between atom C and the midpoint of atoms A and B, while $\theta_C$ is defined to be the angle between atom C, the A-B midpoint and atom A. Note that there are three such coordinate systems, however two of these are related by symmetry, leaving two unique coordinate systems. For the coordinate system in which C is one of the oxygen atoms, energies on a 15x28x18 grid were calculated in which the coordinates vary over the ranges:

$0.8 \leq R_o \leq 8.0$ au

$1.5 \leq R_{so} \leq 4.5$ au

$0 \leq \theta_o \leq 180$.

For the coordinate system in which C is the sulfur atom, energies at a 17x17x10 grid were calculated in which the coordinates vary over the ranges:

$2.4 \leq R_s \leq 8.0$ au

$1.7 \leq R_{oo} \leq 4.5$ au

$0 \leq \theta_s \leq 90$.

The two-body contribution to the total energy at each of these points was evaluated separately (at the same level of theory and at the same diatomic internuclear distances), and
subtracted from the total energy leaving just the three-body contribution. The two, three
dimensional grids of three-body energies were then fit with three-dimensional splines.

The final global expression for the three-body potential was obtained by switching
between the above locally defined functions. The form of the final function is as follows:

\[ V_3(R_1,R_2,R_3) = S_s^*T_s + (1-S_s)^*\{S_a^*T_{oa} + S_b^*T_{ob} - 0.5S_a^*S_b^*(T_{oa}+T_{ob})\} \]

where \( T_s, T_{oa}, \) and \( T_{ob} \) are the three-body terms, expressed in terms of the three dimensional
spline functions, and \( S_s, S_a \) and \( S_b \) are polynomial switching functions that vary between 0.0 and
1.0. The full potential is then simply the sum of this three-body potential and the three, two-
body contributions defined above. Plots showing two dimensional slices through this three
dimensional surface are shown in Figure 1. The FORTRAN code for this potential function can
be obtained from the authors on request.

B. Comparison to Previous Theoretical and Experimental Results

The properties of the various minima, transition states and asymptotes on the current
surface are summarized in Table 1. In this section we compare these results with results from
previous theoretical and experimental studies. First we compare the present results to experiment.
Only the \( \text{OSO} \) minimum has been experimentally characterized. The calculated and observed
vibrational frequencies are in good agreement (calculated: 1230, 1060 and 515 cm\(^{-1}\), observed:
1362, 1151 and 518 cm\(^{-1}\)). Note that the two lowest frequencies are in excellent agreement while
the highest frequency, corresponding to the anti-symmetric stretch, is in error by 130 cm\(^{-1}\). The
energies of the \( \text{SO}+\text{O} \) and \( \text{O}_2+\text{S} \) asymptotes relative to \( \text{SO}_2 \) are also in good agreement with
experiment. For the lowest asymptote, SO+O, the calculated energy is 130.0 kcal mol\(^{-1}\) (including zero point) while the observed bond energy is 130.5 kcal mol\(^{-1}\). For the O\(_2\)+S asymptote, the calculated energy is 135.6 to be compared with an observed energy difference of 136.0.

From the above comparisons we can conclude that the potential reported here is quite accurate both near the SO\(_2\) minimum and near the two lowest asymptotes. Elsewhere the accuracy of the potential is more difficult to judge due to a lack of experimental information. We now compare the energies of the higher lying isomers of SO\(_2\) with other, presumably more accurate, theoretical results. The two most relevant previous calculations are those of Dunning and Raffenetti\(^{14}\) and of Kellogg and Schaefe\(^{15}\). The most accurate calculations from references 14 and 15 place the ring state 101 and 104 kcal mol\(^{-1}\), respectively, above SO\(_2\) or \(-30\) kcal mol\(^{-1}\) higher than in the present calculations. This most likely represents a deficiency in the present calculations stemming from the use of the CASSCF three-body potential. Indeed, the calculations of Dunning \textit{et al}\(^{14}\) suggest that dynamic correlation (neglected in the CASSCF calculations) raise the energy of the ring isomer significantly with respect to SO\(_2\). The agreement between the present calculations and those of references 14 and 15 on the super oxide isomer, SOO, is somewhat better. References 14 and 15 place this isomer 100 and 111 kcal mol\(^{-1}\), respectively, above SO\(_2\), while the present calculations yield an energy difference of 91 kcal mol\(^{-1}\). The present surface and both previous \textit{ab initio} calculations are in agreement as to the ordering of the three minima. Table 1 also gives transition state energies for isomerization between the three isomers. The energies listed, 99 and 107 kcal mol\(^{-1}\), are thus the minimum energies needed to populate the high energy minima, and are therefore of importance to our collisional energy transfer
calculations.

Next, we compare the present global surface to the previous global surface of Murrell et al\textsuperscript{16} (MCVZ). This surface, which is based on \textit{ab initio} calculations similar in quality to Dunning \textit{et al}\textsuperscript{14}, but with adjustments so that the SO\textsubscript{2} dissociation energy matches experiment, places both the ring and superoxide isomers at higher energies (92 and 101 kcal mol\textsuperscript{-1}, respectively) than in the present surface. Probably the most significant difference between the present potential and the MCVZ potential is near the S+O\textsubscript{2} and O+SO asymptotes. The MCVZ surface has no barriers for any of the collinear approaches, i.e. S+OO, O+SO or O+OS, while in the present surface only the O+SO collinear approach is barrier-less, and both the S+OO and O+OS collinear approaches encounter significant barriers. Elsewhere the two surfaces are in reasonable qualitative agreement. Both surfaces predict no barriers for the reactions,

\[
\begin{align*}
S+O\textsubscript{2} & \rightarrow SOO \\
O+SO & \rightarrow OSO \\
O+SO & \rightarrow SOO
\end{align*}
\]

and both surface predict significant barriers for perpendicular S+O\textsubscript{2} and O+SO approaches.

C. Tests of fitted surface

To test the fitted surface, we have calculated rate constants for the S + O\textsubscript{2} bimolecular reaction, and for the O + SO high pressure limit. Standard quasiclassical trajectory methods were used in both cases, using a maximum impact parameter of 8 a\textsubscript{0} for S + O\textsubscript{2} and 10 a\textsubscript{0} for O + SO. For the O + SO collisions, we counted the trajectories as "reactive" if the SO\textsubscript{2} intermediate complex vibrates for at least 10 inner turning points (in the atom-diatom separation). Rate constants were calculated by integrating the cross section over a Boltzmann distribution of
translational energies, and averaging over rotation. An electronic degeneracy factor of 1/27 is applied to both rate constants, thereby assuming that only one of the 27 surfaces available to the reagents can undergo reaction.

For both \( S + O_2 \) and \( O + SO \), we find that the cross sections are very sensitive to the long range part of the potential surface where the potential is within a few kcal mol\(^{-1}\) of the asymptote. Unfortunately, the balance between the two and three body terms is imperfect in this region, and the result is a long range attractive "sphere" around each diatomic that makes the cross sections too large at low energy. To correct for this, we have also calculated results with a modified version of the \( SO_2 \) potential in which the relevant two body potentials are switched smoothly to their dissociation limit wherever the three body term is smaller than 0.6 kcal mol\(^{-1}\) in magnitude. We denote this version of the potential the "truncated" version.

For \( S + O_2 \), our calculated cross section (for the original surface) is \( 140 \, a_0^2 \) for \( E_{\text{trans}} = 0.46 \) kcal mol\(^{-1}\), independent of rotational state. The cross section drops slowly with increasing \( E_{\text{trans}} \) to about \( 90 \, a_0^2 \) at 4.6 kcal mol\(^{-1}\). The resulting rate constant at 300K is \( 9 \times 10^{-12} \, \text{cm}^3/\text{s} \) with little dependence on temperature. The corresponding truncated surface rate constant is \( 5 \times 10^{-12} \, \text{cm}^3/\text{s} \), which indicates the strong sensitivity of the results to the long range nature of the potential surface. Measured values of the rate constant are in the range 1.5-2.8\( \times 10^{-12} \), with the recommended value\(^{17} \) being 2.2\( \times 10^{-12} \, \text{cm}^3/\text{s} \) with essentially no temperature dependence. Clearly the new \( SO_2 \) surface significantly overestimates the rate constant, which confirms that the long range potential is imperfect. An earlier theoretical estimate of the \( S + O_2 \) rate constant due to Craven and Murrell\(^{18} \) produced a much closer 300K value, 1.7\( \times 10^{-12} \, \text{cm}^3/\text{s} \), but there is a significant activation energy (0.5 kcal mol\(^{-1}\)) so the comparison at other temperatures is not as
good.

For O + SO, we find that the cross section is 220 \(a_0^2\) at 0.46 kcal mol\(^{-1}\) energy, independent of SO rotational state, dropping to 100 \(a_0^2\) at 4.6 kcal mol\(^{-1}\). The high pressure rate constant at 300K is 1.4x10\(^{11}\) cm\(^3\)/s, and the corresponding rate constant on the truncated potential is 0.7x10\(^{-11}\). These values are well below the measured value, 5.3x10\(^{-11}\), which is consistent with the conclusion of Cobos et al\(^2\) that more than one electronic state plays a role in the reaction rate. Cobos et al used the statistical adiabatic channel model to estimate rate constants for electronic states that they thought might contribute to the measured result, and concluded that eight surfaces might each contribute values in the range 0.6-0.8x10\(^{-12}\) cm\(^3\)/s. Our value for the original surface is higher than this, but the truncated surface matches it closely. We are not aware of a value for this rate constant from the Craven and Murrell work.

III. Collisional Relaxation Studies

A. Molecular Dynamics Method

In order to characterize the energy transfer dynamics, we applied the SEC (single energy collision) method developed earlier\(^5\). According to this method, a large number of trajectories are integrated, each with the same initial vibrational energy \(E\). The intramolecular phase space of the SO\(_2\) molecule is sampled from a microcanonical ensemble at this energy using the method of Hase et al\(^1\), and the initial conditions for the Ar atom are selected at random from a thermal ensemble at the desired temperature. The initial and final separation was 14 Å in all cases. The maximum impact parameter \(b_{\text{max}}\) was determined using a procedure described elsewhere\(^11\), in which convergence of the integral of \(<\Delta E>\) over impact parameters to within a preset tolerance
is required. In the present calculations, the convergence limit was set to 2% or better.

The initial SO$_2$ rotational energy is sampled from a Boltzmann distribution in which rotational energy is related to angular momentum using a spherical top formula that was previously used by Hippler $et$ $al$. This procedure assumes that molecular rotation is rapidly equilibrated with the bath, which is what we previously observed in detailed studies of CS$_2$ relaxation$^5$. This is different from the procedure of Hippler $et$ $al$, who assumed that the internal part of the SO$_2$ rotational excitation was selected microcanonically on an equal footing with vibration. To test the appropriateness of our method for sampling initial rotation, we performed "successive collisions" calculations$^5$, in which each excited SO$_2$ is subjected to hundreds of successive collisions with Ar. Here the rotational energy is assumed to be thermal before the first collision, just as in the actual experiments, and then subsequently its behavior is determined by the collisions. The calculations show an initial transient of about 10 collisions in which the rotational energy is excited to roughly 1.5 times its thermal value, but this is still well below what would be obtained if rotation where allowed to equilibrate microcanonically with vibration after each collision. Thus it seems that it is more accurate to assume that internal rotation is equilibrated with the bath than with vibration. A consequence of this is that the average energy transfer to rotation that we have calculated is always positive, while that calculated by Hippler $et$ $al$ was always negative. However, the average vibrational energy transfers that we and they have calculated are reasonably close (within 20% at 1000K) for the same potential.

The treatment of rotational energy also proves to be a problem in defining what one means by <$\Delta$E$. Here we have followed the procedure of Hippler $et$ $al$, who used the spherical top formula to define rotational energy after each collision, and then the vibrational energy is
equated to the difference between internal and rotational energy. This procedure has the advantage that it uses an easily calculated constant of the motion, namely the magnitude of the rotational angular momentum, to define rotational energy. We tried other methods, such as using the time-averaged rigid-rotor energy, which do not use rigorous constants of the motion, and found that these give spurious results due to vibration/rotation coupling that occurs in the absence of collisions.

For calculations involving the \textit{ab initio} intramolecular potential, the method of sampling of the initial intramolecular phase space may fail because it was developed for a single-well potential. In order to test this, we examined collisions in which selection of the initial conditions for vibrational motion was based on using the SO0 isomer of the \textit{ab initio} potential surface.

All of our calculations are fully classical in the sense that there was no attempt to mimic quantum behavior. The "excitation energy" in SO$_2$ is therefore measured from the bottom of the SO$_2$ well and the notion of zero-point energy is not introduced. Fortunately, the zero-point energy in SO$_2$ is low relative to the excitation energies of interest here, so the ambiguity in energy scales is not large. We have previously noted\textsuperscript{5} that "detailed balance" cannot be maintained in the simulations unless a purely classical calculation is done, so it is not possible (within the framework of the classical theory) to determine the errors resulting from the use of classical mechanics.

B. Intra- and Intermolecular Potential

We have considered both the intramolecular potential developed by Hippler \textit{et al.}\textsuperscript{4} and the original \textit{ab initio} potential in our calculations. (A few calculations using the truncated \textit{ab initio} surface indicated that its energy transfer properties are the same as for the original surface.
so we didn't pursue this further.) Throughout this work, we shall refer to the two surfaces as "3-Morse" and "ab initio", respectively. The normal mode frequencies, which provide important properties of a molecule in the context of energy transfer, are 394, 1187, and 1213 cm\(^{-1}\) on the 3-Morse surface and 515, 1060, and 1230 cm\(^{-1}\) on the ab initio surface for the bend, asymmetric stretch and symmetric stretch modes, respectively. The dissociation energy to O + SO is 130.5 kcal mol\(^{-1}\) on the 3-Morse potential, in good agreement with the 132.5 kcal mol\(^{-1}\) value (not including zero point energy) on the ab initio surface, but the corresponding S + O\(_2\) dissociation energies are significantly different, being 200 and 137.4 kcal mol\(^{-1}\), respectively. The trajectory calculations are about a factor of 20 faster for calculations based on the 3-Morse surface.

We studied the effect of several forms of the intermolecular potential on the energy transfer. Most of our calculations have been based on pairwise Lennard-Jones potentials, as these proved successful in our earlier work. Fig. 2 shows the Ar-O and Ar-S potentials that we have used. The Lennard-Jones parameters are identical with those for Ar-Ne and Ar-Ar as taken from the literature\(^{20}\). (We shall refer to this set of parameters as the "rare gas Lennard-Jones (RGLJ) model"). The figure also shows the potential curves obtained with the small (SLJ) and large (LLJ) Lennard-Jones parameters from Hippler et al.\(^ {4}\) (Note that in this approximation there is no distinction between Ar-O and Ar-S). Evidently, the RGLJ potential is intermediate between LLJ and SLJ, which is probably more realistic.

C. Results

Figure 3 shows the average vibrational energy transfer \(<\Delta E>\) from SO\(_2\) at various impact parameters using different intermolecular potentials at 300K as obtained with the 3-Morse intramolecular SO\(_2\) potential. This figure shows that for small impact parameters, the absolute
value of \(<\Delta E>\) is largest for the SLJ model, and smallest for the LLJ. At large impact parameters the SLJ results drop off most quickly and the LLJ most slowly. The RGLJ results are consistently in-between the others. The \(b_{\text{max}}\) necessary for converged calculations is 3.0, 6.0 and 8.0 Å for the SLJ, RGLJ and LLJ models, respectively. Similar results are obtained for the \(ab \text{ initio} + \text{RGLJ}\) potential, and we find that the optimum \(b_{\text{max}}\) is 5.5 Å at 300K and 4.5 Å at 1000K.

Figure 4 shows the energy dependence of the \(<\Delta E>\) for the various intermolecular potentials and the 3-Morse intramolecular potential. For all the results, \(<\Delta E>\) was scaled to a common \(b_{\text{max}}\) of 5.5 Å. The figure shows that \(-<\Delta E>\) increases monotonically with \(E\), with a slope which increases rapidly with \(E\) close to the dissociation energy. The SLJ and RGLJ potentials give nearly identical \(<\Delta E>\)'s, presumably due to an accidental cancellation between the magnitude and range of the \(<\Delta E>\) results in Fig. 3. The LLJ potential, with its much longer range in Fig. 3, leads to higher \(<\Delta E>\)'s than the others by a factor of 1.5 to 2. This has also been observed by Hippler et al.

The influence of the intramolecular potential on \(<\Delta E>\) is shown in Fig. 5, where we plot \(<\Delta E>\) vs. \(E\) for the 3-Morse and \(ab \text{ initio}\) models. Some representative values are listed in Table 2. Again, the average values were scaled to a common \(b_{\text{max}}\) of 5.5 Å. Throughout the entire energy range, \(<\Delta E>\) is lower for the \(ab \text{ initio}\) potential by a factor of 1.5 to 3. This may be a consequence of the smaller frequency of the bend mode on the \(ab \text{ initio}\) potential. In a study addressing this question\(^4\), the energy transfer from highly excited CS\(_2\) was found to be very sensitive to the bend frequency, the absolute value of the \(<\Delta E>\) increasing with decreasing frequency.

Fig. 5 shows that the energy dependence of \(<\Delta E>\) is qualitatively the same for both
intramolecular potentials, though there are quantitative differences. Roughly speaking, the dependence of \(\langle \Delta E \rangle\) on \(E\) can be thought of as linear at low excitation energies, then increasing to faster than quadratic at high excitation. A log-log plot of the results is presented in Fig. 6, and this shows that the change from linear to quadratic takes place smoothly at about 50-90 kcal mol\(^{-1}\) excitation. Note that the results for the \textit{ab initio} potential seem to change smoothly for energies near to 100 kcal mol\(^{-1}\) excitation where the ring and SOO minima become accessible on the potential surface. This indicates that the multiple well nature of the potential surface does not cause a qualitative difference in the energy transfer dynamics.

Included in Fig. 5 is \(\langle \Delta E \rangle\) for trajectories sampled using the SOO minimum as reference equilibrium geometry. The difference between the "SO\(_2\)-sampled" and "SOO-sampled" \(\langle \Delta E \rangle\)'s is relatively small at 300K but larger at 1000 K where the "SOO-sampled" results are smaller. This indicates (1) that the phase space sampling method we are using is unable to sample uniformly the phase space of a highly anharmonic molecule and (2) that the motion in the internal phase space of SO\(_2\) is not completely randomized.

The energy transfer probability distributions calculated with the 3-Morse and \textit{ab initio} intramolecular potentials at 1000K and \(E = 125\) kcal mol\(^{-1}\) are plotted in Figure 7. This shows that the "up" branch probabilities are more-or-less the same, while the "down" branch probabilities are larger for the 3-Morse potential than for the \textit{ab initio} model. This difference in the down branch makes the 3-Morse potential have more negative average energy transfers as noted in Fig. 5. Both the up- and especially the down wings of the distribution exhibit long tails extending to \(\langle \Delta E \rangle = 12\) kcal mol\(^{-1}\) on the up- and \(\langle \Delta E \rangle = -35\) kcal mol\(^{-1}\) on the down. This means that there is a finite probability of transferring large amounts of energy in a single collision.
Such "supercollisions" have been found both in the experiments and earlier theoretical work\textsuperscript{22,23}, and the present results are similar to what was seen for CS\textsubscript{2}\textsuperscript{22}.

The calculated $\langle \Delta E \rangle$'s are compared to the limited number of experimental data in Table 2. All the results have been consistently normalized to the same gas kinetic collision rate, namely that for $b_{\text{max}} = 5.5$ Å. The agreement is excellent at 1000K for the $ab\ initialo + RGLJ$ potential results. At 300K, however, the calculated values are higher than experiment by factors of 3 to 7. These comparisons are similar to previous results that we have obtained for the relaxation of CS\textsubscript{2}\textsuperscript{7} by rare gases, but it is unknown why low and high temperatures behave so differently. We do know that uncertainties in the intramolecular potential can cause factor-of-two changes in $\langle \Delta E \rangle$, so this provides a realistic estimate of the error (other than statistical) that can occur in our theoretical results. The experimental results have a similar uncertainty associated with them, so the combined error of theory and experiment could conspire to explain the discrepancy. There are, however, additional sources of uncertainty in both experiment and theory, so in many respects it is extremely encouraging that the agreement is as good as it is.

The rate of change of $\langle \Delta E \rangle$ with $E$ is also different between experiment and theory. In the experiments an almost perfect quadratic dependence was observed, especially at low excitation\textsuperscript{1}. Our calculations show a transition between almost linear at low excitation and quadratic or faster at high excitation. In spite of this difference, the comparison between measured and calculated $\langle \Delta E \rangle$'s is of comparable quality at both low and high energies. This suggests that the extrapolation used by Cobos et al to relate the direct values of $\langle \Delta E \rangle$ measured at low energies to the indirect values at high energies is not seriously in error.
IV. Conclusion

In the present study we have developed a global \textit{ab initio} surface for the SO\textsubscript{2} molecule that has accurate structural and vibrational properties near the SO\textsubscript{2} minimum, dissociates correctly, and is realistic for energies up to where isomers like SOO and ring SO\textsubscript{2} are significant. We tested this surface by studying the S + O\textsubscript{2} reaction dynamics, and by calculating the O + SO high pressure rate constant. Both tests indicate that the many-body expansion approach produces a surface that is too attractive at long range where the energy is within a few kcal mol\textsuperscript{-1} of dissociation. However this deficiency doesn't seem to influence the energy transfer properties that we have studied.

Our studies of the collisional relaxation of SO\textsubscript{2} in an Ar bath show that the \textit{ab initio} SO\textsubscript{2} potential has significantly smaller \langle\Delta E\rangle's than the simpler 3-Morse potential at all energies. This effect, plus the use of a more realistic intermolecular potential, leads to \langle\Delta E\rangle's that are in reasonable agreement with the direct experiments, especially at 1000K.

Our results also indicate that \langle\Delta E\rangle increases linearly with E for low energies, but within 30 kcal mol\textsuperscript{-1} of dissociation, the energy transfer becomes much more efficient, and the dependence of \Delta E on E is even stronger than quadratic. Both the \textit{ab initio} and 3-Morse potentials exhibit similar functional dependence on E, which indicates that the secondary minima do not influence energy transfer behavior in a distinct way. Close to the dissociation threshold, the new results are in better agreement with experiment than previous theory, but it is still necessary to include for the influence of excited electronic states to explain the recombination rate measurements.
V. Acknowledgements

This research was supported by the Department of Energy, Division of Chemical Sciences, under Contract W-31-109-Eng-38, by NSF grant CHE-9016490, by the Hungarian National Research Fund grant OTKA-T7428, and by the US-Hungarian Joint Fund grant JF411. We thank Stephanie Halstead for help with the calculations.
References


Table 1. Calculated Energies (kcal mol\(^{-1}\)), Geometries (Å) and Frequencies (cm\(^{-1}\)) for the Minima and Transition States on the SO\(_2\) Surface.

<table>
<thead>
<tr>
<th></th>
<th>R(_1)</th>
<th>R(_2)</th>
<th>R(_3)</th>
<th>(\omega_1)</th>
<th>(\omega_2)</th>
<th>(\omega_3)</th>
<th>Relative energy(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minima:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OSO</td>
<td>1.45</td>
<td>1.45</td>
<td>2.48</td>
<td>1230</td>
<td>1060</td>
<td>515.</td>
<td>0.0(0.0)</td>
</tr>
<tr>
<td>SOO</td>
<td>1.61</td>
<td>2.40</td>
<td>1.29</td>
<td>1210</td>
<td>905</td>
<td>425.</td>
<td>91.0(90.6)</td>
</tr>
<tr>
<td>Ring</td>
<td>1.69</td>
<td>1.69</td>
<td>1.46</td>
<td>1055</td>
<td>835</td>
<td>725.</td>
<td>73.0(72.7)</td>
</tr>
<tr>
<td>SO + O</td>
<td>1.52</td>
<td></td>
<td></td>
<td>1055</td>
<td></td>
<td></td>
<td>132.5(130.0)</td>
</tr>
<tr>
<td>O(_2) + S</td>
<td>1.21</td>
<td></td>
<td></td>
<td>1565</td>
<td></td>
<td></td>
<td>137.4(135.6)</td>
</tr>
</tbody>
</table>

|       |         |         |         |             |             |             |                     |
| Transition States: |         |         |         |             |             |             |                     |
| OSO \(\rightarrow\) Ring | 1.61 | 1.61    | 1.82    | 1060        | 715         | 1165.i      | 99.1(97.6)         |
| Ring \(\rightarrow\) SOO | 1.62 | 2.12    | 1.37    | 1090        | 910         | 890.i       | 106.8(105.9)       |

\(^a\)Numbers in parenthesis include a harmonic estimate of the zero point energy.
Table 2. Average Energy Transfer$^a$ at 300K and 1000K.

<table>
<thead>
<tr>
<th>Temperature:</th>
<th>300K</th>
<th>1000K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy, kcal mol$^{-1}$</td>
<td>57</td>
<td>130</td>
</tr>
</tbody>
</table>

- 3-Morse, RGLJ: -0.49, -2.45, -0.61, -2.48
- $ab$ initio, RGLJ: -0.20, -1.0, -0.42, -1.45
- experiment$^1$: -0.03, -0.16, -0.45, -1.0

$^a$Scaled to a common $b_{\text{max}}$ of 5.5 Å.
Figure 1  Contour plots for: (a) the movement of S around O2, and (b) the movement of O around SO. In each case the diatomic fragment is kept fixed at its equilibrium geometry. The contour interval is 5 kcal mol⁻¹. Dashed contours denote regions lower in energy than the respective atom plus diatom dissociation limit. Solid contours denote higher energy regions.

Figure 2  Pair potentials used to construct the Ar-SO₂ intermolecular potential.

Figure 3  <ΔE> as a function of the impact parameter for the 3-Morse intramolecular and various models of the intermolecular interaction at 300 K. Squares: RGLJ; circles: SLJ; diamonds: LLJ.

Figure 4  Energy dependence of <ΔE> for the 3-Morse intramolecular and various models of the intermolecular interaction at 1000 K. Squares: RGLJ; circles: SLJ; diamonds: LLJ.

Figure 5  Energy dependence of the <ΔE> for the 3-Morse + RGLJ model (open circles) and ab initio + RGLJ model (filled circles) at (a) 300K and (b) 1000K. Also shown are results for the SOO molecule (triangles) for ab initio + RGLJ model.

Figure 6  <ΔE> vs. E on a log-log scale at 300 K (open symbols) and 1000 K (filled symbols); circles: 3-Morse potential; squares: ab initio potential.

Figure 7  The energy transfer probability distribution obtained at 125 kcal mol⁻¹ excitation as obtained with the 3-Morse (continuous line) and the ab initio potential (dashed line) at 1000 K.
Fig. 5.