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# Photodissociation of the $SO_2 \cdot SO_2^+$ dimer in the visible region of the spectrum: Product relative kinetic energy distributions and product angular distributions

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The results of an investigation of the photodissociation of the  $SO_2 \cdot SO_2^+$  cluster ion in the visible wavelength range (458-590 nm) are presented. The studies were performed using a crossed fast ion beam/laser beam experiment. Product relative kinetic energy distributions and product center of mass angular distributions are reported. Methods used to extract the angular distributions from the experimental measurements are described. The only ionic product observed from the photodissociation of  $SO_2 \cdot SO_2^+$  was  $SO_2^+$ . The product relative kinetic energy distributions are characteristic of statistical energy disposal. However, statistical phase space theory substantially overestimates the fraction of available energy partitioned into relative kinetic energy. The product angular distributions are discussed in terms of the asymmetry parameter  $\beta$ .  $\beta$ increases with the products relative velocity. A simple phase space theory model for  $\beta$  is developed for statistical dissociation with complete rotational averaging. The model accounts for the variation of  $\beta$  with the products relative velocity.  $\beta$  also varies with wavelength. The variation of  $\beta$ with wavelength is ascribed to changes in the lifetime of the cluster. At 458 nm the values of  $\beta$ indicate that complete rotational averaging has not occurred. At 590 nm the data are consistent with complete rotational averaging, implying a lifetime > 5 average rotational periods. The results are interpreted in terms of a transition to a low lying bound excited state of the SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> cluster which arises from one of the low lying excited states of  $SO_2^+$  and the ground state of  $SO_2$ .

### **I. INTRODUCTION**

Almost all simple ion-molecule dimers (e.g.,  $N_2 \cdot N_2^+$ and NO·NO<sup>+</sup>) photodissociate in the visible region of the spectrum.<sup>1-5</sup> In contrast, neutral van der Waals dimers generally do not adsorb strongly in this region of the spectrum. The origin of this difference is quite straightforward. Combination of an ion with the corresponding molecule generally gives rise to twice as many states as combination of two identical molecules in their ground states.<sup>6</sup> For example,  $N_2({}^{1}\Sigma_{g}^{+}) + N_2({}^{1}\Sigma_{g}^{+})$  gives rise to a single  ${}^{1}\Sigma_{g}^{+}$  state in a linear geometry but  $N_2^+({}^{2}\Sigma_{g}^{+}) + N_2({}^{1}\Sigma_{g}^{+})$  yields two  ${}^{2}\Sigma$ states, one bound and one repulsive.<sup>7</sup> Ion-molecule dimers are quite strongly bound (0.5–1.0 eV) so that a transition from the ground state to one or more repulsive states can usually occur in the visible region of the spectrum.

In a recent series of papers<sup>3-5</sup> we have reported the results of investigations of the photodissociation dynamics of dimer ions such as NO·NO<sup>+</sup>, N<sub>2</sub>·N<sub>2</sub><sup>+</sup>, and CO<sub>2</sub>·CO<sub>2</sub><sup>+</sup>. These dimer ions photodissociate in the visible region of the spectrum by a direct transition to a repulsive surface, although for CO<sub>2</sub>·CO<sub>2</sub><sup>+</sup> a minor product component arises from a different mechanism which could be internal conversion followed by vibrational predissociation. This later result implicates the involvement of a long lived bound excited state in the CO<sub>2</sub>·CO<sub>2</sub><sup>+</sup> dimer. Such a state would have to have a bond energy greater than 2.3 eV if it were to correlate to the lowest energy excited state in the products:  $CO_2^+(\tilde{A} \ {}^2\Pi)$  and  $CO_2(\tilde{X} \ {}^1\Sigma_g \ {}^+)$ . As a consequence we could not be certain a bound excited state of  $CO_2 \cdot CO_2^+$  was involved.<sup>5</sup>

In this paper we report the results of an investigation of the photodissociation dynamics of the  $SO_2 \cdot SO_2^+$  cluster.

Unlike  $CO_2^+$ ,  $SO_2^+$  has several low lying excited electronic states which means that the  $SO_2 \cdot SO_2^+$  cluster will have low lying excited electronic states which may be bound. The motivation for the present study was to determine if these low lying excited electronic states play any role in the photochemistry of the  $SO_2 \cdot SO_2^+$  cluster.

The rest of this paper is organized as follows: In the next section we briefly review our crossed fast ion beam/laser beam experiment. This is followed by Sec. III where we also describe the methods used to extract detailed information on the product angular distributions from the experimental measurements. The results are discussed in Sec. IV where phase space theory calculations of the product relative kinetic energy distributions and product angular distributions are reported. The paper ends with a brief Conclusions.

## **II. EXPERIMENTAL**

The experiment, which has been described in detail elsewhere,<sup>3,4</sup> consists of a reverse geometry mass spectrometer (VG Instruments, ZAB-2F) and an argon ion laser (Coherent, Innova 20) and broadband cw dye laser (Coherent, model 590). A schematic diagram of the experimental apparatus is shown in Fig. 1.

Cluster ions were generated by the association reaction

$$SO_2^+ + SO_2 + M \rightarrow SO_2 \cdot SO_2^+ + M, \tag{1}$$

in a cooled ( $\sim 297$  K), high pressure ion source. A mixture of 40%-50% SO<sub>2</sub> (Linde, Anhydrous Grade) in N<sub>2</sub> (liquid boiloff) was used at a total pressure of 0.10-0.11 Torr. Ions effusing from the source were accelerated to 8 kV, mass selected by the magnet, brought to a spatial focus and crossed with a focused laser beam. The products were energy analyzed by

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FIG. 1. Schematic diagram of the experimental apparatus. Note that the laser beam is actually along the z axis (vertical) as it intersects the ion beam.

an electrostatic analyzer (ESA) which also performs a mass analysis of the products. An energy resolving power of 2000 FWHM was used. The laser beam was modulated and updown pulse counting techniques were employed to subtract out the background signal. The background signal was quite large, around 10<sup>3</sup> cps (approximately 1/5 of the photodissociation signal). With the conditions employed this large background signal probably arises mainly from the unimolecular dissociation of clusters excited in the source region of the instrument ("metastables") rather than collision induced dissociation in the second field free region. Even thermal clusters contain substantial amounts of internal energy (because of the low frequency cluster modes) so some of the background signal could arise from a thermally activated unimolecular reaction. Most of the background signal, however, probably arises from the unimolecular dissociation of the small fraction of clusters collisionally activated in the acceleration region.

Experiments were performed using the individual argon ion laser lines at 514, 488, and 458 nm and at 590 nm using the dye laser with R6G dye. The laser beams from both the dye laser and the ion laser are plane polarized. Measurements were performed with the laser beam polarization at 0° and 90° with respect to the ion beam direction and at the "magic angle" of 54.7°.<sup>4</sup> The angle between the laser beam polarization and the ion beam direction was changed using a polarization rotator (Spectra Physics, 310A).

Collision induced dissociation spectra were recorded by leaking He into a collision cell located between the magnet and the ESA. Spectra were recorded with a main beam attenuation of 30%.

### **III. RESULTS**

Some relevant thermochemical data<sup>8-10</sup> are summarized in Table I. The  $SO_2 \cdot SO_2^+$  cluster is bound by 0.66 eV relative to  $SO_2^+ + SO_2$ .<sup>9</sup> Two other sets of products are energetically accessible from the ground state of the  $SO_2 \cdot SO_2^+$  cluster with photon energies employed. These are  $SO^+ + SO_3$ , at an energy 0.07 eV above the  $SO_2^+ + SO_2$  products, and  $SO_3^+ + SO$  at ~0.7 eV above  $SO_2^+ + SO_2$ . However, neither of these products were detected. The only product observed from the photodissociation of the  $SO_2 \cdot SO_2^+$  cluster was  $SO_2^+$ .

The collisional induced dissociation spectrum of the  $SO_2 \cdot SO_2^+$  cluster is given in Table II. The only fragment ions with intensity over 1% of the total are  $SO \cdot SO_2^+$  (m/z 112),  $SO_2^+$  (m/z 64), and  $SO^+$  (m/z 48). The most intense fragment is  $SO_2^+$  (78%). This is consistent with a structure of two loosely bound  $SO_2$  moieties for the cluster.

#### A. Product kinetic energy distributions

As described in detail in Ref. 4, product relative kinetic energy distributions are derived from peak shapes measured with the electric vector of the laser beam at the magic angle of 54.7° with respect to the ion beam direction. Figure 2 shows the product relative kinetic energy distributions measured at 590 and 458 nm. The distributions peak at close to zero relative kinetic energy and the probability falls off roughly exponentially with increasing kinetic energy. These kinetic energy distributions have a different shape from those we have measured for the photodissociation of other dimer ions such as NO·NO<sup>+</sup>,  ${}^{3}N_{2}\cdot N_{2}^{+4}$  and CO<sub>2</sub>·CO<sub>2</sub><sup>+</sup>. <sup>5</sup> For those clusters the distributions peaked at much larger values of relative kinetic energy (~0.2–0.7 eV) and were roughly

TABLE I. Heat of formation of the cluster ion and possible products.

· · · · · · · · · · · · · · · · · · ·	$\Delta H_{f0}^{0}(\mathrm{eV})^{\mathrm{a}}$	
SO <sub>2</sub> ·SO <sub>2</sub> +	5.57	
$SO_2^+ + SO_2$	6.23	
$SO^+ + SO_1$	6.30	
$SO_3^+ + SO_1^-$	~6.95	

<sup>a</sup> From Refs. 8–10.

TABLE II. Collision induced dissociation spectrum of the  $SO_2 \cdot SO_2^+$  cluster.<sup>•</sup>

<i>m/z</i> <sup>∎</sup>	Ionic product	Normalized intensity
112	\$ <sub>2</sub> O <sub>3</sub> <sup>+</sup>	2.5
96	SO <sub>4</sub> <sup>+</sup>	0.4
80	SO <sub>3</sub> <sup>+</sup>	0.4
64	SO <sub>2</sub> <sup>+</sup>	78
48	SO <sup>+</sup>	18
32	S <sup>+</sup> , O <sub>2</sub> <sup>+</sup>	0.9
16	O+	< 0.05

<sup>a</sup>The <sup>32</sup>S isotope was exclusively selected in the SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> cluster.

triangular in shape. Distributions of this shape are characteristic of dissociation on a repulsive surface. Kinetic energy distributions of the shape shown in Fig. 2 for  $SO_2 \cdot SO_2^+$  are characteristic of statistical energy disposal.

Figure 3 shows a plot of the average product relative kinetic energy against the available energy. Assuming that the products are formed in their ground electronic states, the available energy is given by

$$E_{\rm AV} = h\nu - D_0^0(\rm SO_2 - SO_2^+) + E_{\rm INT}, \qquad (2)$$

where hv is the photon energy and  $E_{\rm INT}$  is the initial internal energy in the SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> cluster. With the ion source conditions employed most of the cluster ions will undergo sufficient collisions for their internal energy to be brought close to thermal. The solid line drawn through the data points is a linear least squares fit. The average product kinetic energy apparently increases linearly with the available energy. The equation for the line is

$$\langle E_t \rangle = 0.065(\pm 0.003) + 0.048(\pm 0.001)E_{\rm AV},$$
 (3)

where the numbers in brackets are the standard deviations.

# **B. Product angular distributions**

For an electric dipole transition photon absorption arises from an interaction between the electric vector of the photon and the transition dipole moment of the molecule. Photon adsorption occurs preferentially when the electric



FIG. 2. Product relative kinetic energy distributions measured for the photodissociation of  $SO_2$ : $SO_2^+$  at 458 and 590 nm.



FIG. 3. Plot of the average relative kinetic energy against the available energy for the photodissociation of  $SO_2 \cdot SO_2^+$ . The points are the experimental data, the solid line is a least squares fit to the experimental data, and the dashed lines are the result of statistical phase space theory calculations (see the text).

vector and transition dipole moment are aligned. Thus an anisotropic distribution of excited molecules is generated and on dissociation this anisotropic distribution is reflected in the product angular distributions. The photoproduct angular distributions can provide information about the lifetime of the photoexcited molecule and also information about the nature of the electronic transition.<sup>11–13</sup>

In our experiment a high energy ion beam is crossed with a laser beam and the products are analyzed by an electrostatic analyzer (ESA). The ESA measures essentially<sup>14</sup> the energy along the ion beam direction. Peak shapes measured with the laser polarization at the magic angle of 54.7° with respect to the ion beam direction contain no information about the product angular distribution.<sup>4</sup> Peak shapes measured with other orientations of the laser beam polarization will reflect the products angular distribution. For example, if the products recoil along the transition dipole moment then a broader peak shape would be measured with the electric vector along the ion beam direction than with the electric vector perpendicular to the ion beam direction. Obtaining the product angular distributions from these 0° and 90° peaks is not straightforward because the peak shapes are a convolution of the product angular distribution and product relative kinetic energy distribution. The analysis is further complicated by instrumental discrimination. Some of the products with a large velocity component perpendicular to the ion beam direction are lost due to the finite detector slit height and  $\alpha$  slit<sup>15</sup> width. For SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> the product relative kinetic energies are small and trial calculations indicated that there was no significant instrumental discrimination.

The photoproduct angular distribution has the general form<sup>11,16</sup>

$$P(\theta) = (4\pi)^{-1} [1 + \beta P_2(\cos \theta)],$$
(4)

where  $P(\theta)$  is the probability that the products recoil into a solid angle  $d\omega$  at an angle  $\theta$  with respect to the electric vector,  $P_2(\cos \theta)$  is the second degree Legendre polynomial in  $\cos \theta$ , and  $\beta$  is the asymmetry parameter which can have values between +2 and -1.

In our previous work information about the product angular distributions was derived from the 0° and 90° peak shapes using an iterative fitting procedure. Peak shapes were calculated using the measured product relative kinetic energy distribution and the product angular distribution given by Eq. (4). The calculated peak shapes were compared with the measured ones and  $\beta$  was adjusted to fit the measured peaks. This procedure is tedious, somewhat subjective and the result can be ambiguous if  $\beta$  varies with the product relative kinetic energy (see Ref. 17 for an example). What is required is a procedure to directly and unambiguously extract  $\beta$  as a function of the product relative kinetic energy from the measured peak shapes. Here we present a method to accomplish this.

The probability that the products recoil at an angle  $\theta'$ with respect to the ion beam direction is<sup>4</sup>

$$P(\theta',\chi) = \sin \theta' [1 + \beta P_2(\cos \theta')P_2(\cos \chi)], \qquad (5)$$

in which  $\chi$  is the angle between the ion beam direction and the laser beam polarization. It follows that for a single value of product relative kinetic energy release the probability that the products have a resultant velocity along the ion beam direction of  $U_x$  in the center of mass reference frame is

$$P(U_{x},\chi) = U^{-1} \left[ 1 + \frac{\beta}{2} \left\{ \frac{3U_{x}^{2}}{U^{2}} - 1 \right\} P_{2}(\cos \chi) \right], \quad (6)$$

where U is the velocity of the product ion at angle  $\theta'$  to the x direction in the center of mass reference frame. (Note  $\cos^2 \theta' = U_x^2/U^2$  in the c.m. reference frame). In the laboratory frame the energy measured by the ESA is to a good approximation<sup>18</sup>

$$E \simeq \frac{1}{2} m_2 V_0^2 + \frac{1}{2} m_2 V_0 U_x, \tag{7}$$

in which  $V_0$  is the laboratory velocity of the reactant ions and  $m_2$  is the mass of the product ion. Since *E* is proportional to  $U_x$ , the product ion peak shape in the laboratory frame is given by

$$P(E,\chi) \simeq P(U_x,\chi) = U^{-1} \left[ 1 + \frac{\beta}{2} \left\{ \frac{3U_x^2}{U^2} - 1 \right\} P_2(\cos \chi) \right]$$
(8)

and for a distribution of product relative kinetic energies the peak shape is

$$P(E,\chi) = \int_{U_{\chi}}^{\infty} dU P(U) U^{-1} \left[ 1 + \frac{\beta(U)}{2} \times \left\{ \frac{3U_{\chi}^{2}}{U^{2}} - 1 \right\} P_{2}(\cos \chi) \right],$$
(9)

where P(U) is the product center of mass velocity distribution. To analyze the peak shapes it is useful to consider the quantity  $P(E,0^\circ) - P(E,90^\circ)$ , which is given by

$$P(E,0^{\circ}) - P(E,90^{\circ}) = \frac{3}{2} \int_{U_{x}}^{\infty} dU P(U) U^{-1} \frac{\beta(U)}{2} \\ \times \left\{ \frac{3U_{x}^{2}}{U^{2}} - 1 \right\}.$$
 (10)

Using a polynomial approximation for  $\beta(U)$ :

$$\beta(U) = \beta_0 + \beta_1 U + \beta_2 U^2 + \cdots,$$
(11)

information on the product angular distributions can be obtained by fitting Eq. (10) to the measured peak shapes using a least square procedure to determine the coefficients in Eq. (11). This is most readily accomplished using matrix methods.<sup>19</sup>

The results of this analysis are shown in Fig. 4 where the values of  $\beta$  derived using a fifth order polynomial are plotted against the product ion velocity relative to the center of mass. A fifth order polynomial was judged to be sufficiently "flexible" to follow the gross real features. The values of the asymmetry parameter are probably unreliable at the extremes of the plotted velocity range because the signal to noise at these velocities is small. Figure 5 shows the 0° and 90° peak shapes for the 514 nm line. The points are the experimental data and the lines are the result of the theoretical analysis. It is evident that the 0° and 90° peak shapes are not very different, indicating that the product angular distributions are not very anisotropic. Consequently the values for the asymmetry parameter  $\beta$  shown in Fig. 4 are fairly small,



FIG. 4. Plot of the asymmetry parameter  $\beta$  of the product angular distributions against the product center of mass velocity (a relative kinetic energy scale is also shown). The solid lines are the experimental data and the dashed lines are the result of statistical phase space theory calculations assuming complete rotational averaging (see the text).



FIG. 5. Peak shapes measured for the photodissociation of  $SO_2 \cdot SO_2^+$  at 514 nm with the laser polarization at 0° and 90°, with respect to the ion beam direction. The points are the experimental data and the lines the result of the theoretical analysis described in the text.

around 0.25. From Fig. 4 it can be seen that the asymmetry parameter increases slightly with product velocity for all wavelengths studied. This indicates that the product angular distributions become more anisotropic as the velocity relative to the c.m. increases. Also, as can be seen from Fig. 4, the asymmetry parameter at a given velocity increases slightly with photon energy.

# **IV. DISCUSSION**

Unfortunately there is no information available on the structures and electronic configurations of the ground state and the low lying excited electronic states of the  $SO_2 \cdot SO_2^+$  dimer ion. The ground states of  $SO_2^6$  and  $SO_2^{+20}$  are  ${}^1A_1$  and  ${}^2A_1$ , respectively. Combining these states will generate two doublet states owing to resonance mixing.<sup>6</sup> At least one of these states must be bound and the other is probably repulsive. The first excited  $\tilde{a} \, {}^3B_1$  state of  $SO_2^+$  has two low lying excited states: the  $\tilde{A} \, {}^2A_2$  state at 0.71 eV above the ground state and the  $\tilde{B} \, {}^2B_2$  state at 0.94 eV.<sup>21</sup> Combination of each of these states with  $SO_2 \tilde{X} \, {}^1A_1$  will generate two doublet states. One or more of these states may be bound.

There are several possible mechanisms by which photodissociation of  $SO_2 \cdot SO_2^+$  could occur. One possible mechanism is a direct transition to one or more of the repulsive states which correlate to either ground or excited state products. A direct transition to a repulsive surface would be expected to result in the partitioning of a substantial fraction of the available energy into relative kinetic energy. In addition, the lifetime of the excited cluster would be less than a rotational period, resulting in anisotropic angular distributions. Alternatively, the transition could be to a bound excited state which correlates with either the  $SO_2^+ \tilde{A}$  or  $\tilde{B}$  states. Since these states are quite low in energy the transition would be to highly vibrationally excited quasibound levels of the excited state. Dissociation could occur directly from this excited state by vibrational predissociation (statistical unimolecular dissociation) or a rapid internal conversion to the ground state could occur, followed by vibrational predissociation. Vibrational predissociation would be expected to result in statistical energy disposal with a small fraction of the available energy partitioned into relative kinetic energy. Depending on the rate of dissociation, the lifetime of the excited cluster could be longer than a rotational period so the product angular distributions may show the results of rotational averaging.

As noted in Sec. III the shape of the product relative kinetic energy distributions is characteristic of statistical energy disposal. It will obviously be instructive to compare the measured distributions with the predictions of statistical phase space theory. For products with total energy E and total angular momentum J the probability that the products have a relative kinetic energy  $E_t$  is<sup>22</sup>

$$P(E,J;E_t) = \frac{\int dE_r \rho_v(E - E_t - E_r) \int \int dL \, dJ_r \, \rho_r(E_r,J_r)}{\int dE_{tr} \, \rho_v(E - E_{tr}) \Gamma_{ro}(E_{tr},J)},$$
(12)

in which  $\rho_v$  and  $\rho_r$  are the vibrational and rotational densities of states,  $\Gamma_{ro}$  is the rotation-translational sum of states,  $E_r$  and  $E_{tr}$  are the rotational and rotational plus translational energies respectively,  $J_r$  is the products total rotational angular momentum, and L is the products orbital angular momentum. Assuming that the products are in their ground electronic states calculations were performed using an energy

$$E = hv - D_0^0 (SO_2^+ - SO_2) + E_{\rm th}, \qquad (13)$$

where  $E_{\rm th}$  is the average thermal internal energy. Finally the probabilities given by Eq. (12) were averaged over a classical thermal angular momentum distribution:

$$P(J) = (2J)^{2} \exp(-BJ^{2}/k_{B}T) / \int_{0}^{\infty} dJ (2J)^{2} \\ \times \exp(-BJ^{2}/k_{B}T).$$
(14)

The parameters used in the calculations are summarized in Table III. Most of the required parameters were available

TABLE III. Parameters used in the phase space calculations.

	SO <sub>2</sub>	SO <sub>2</sub> <sup>+</sup>	<u> </u>
$\overline{v_i(\mathrm{cm}^{-1})^*}$	11518	900 <sup>k</sup>	
	518	403 <sup>k</sup>	
	1362	1200 <sup>1</sup>	
$B_i(\mathrm{cm}^{-1})^{\mathrm{b}}$	0.589#	0.685 <sup>m</sup>	
$\alpha(Å^3)^c$	3.72 <sup>h</sup>		
$\mu(amu)^d$	32		
$D_0^0(eV)^e$	0.66 <sup>i</sup>		
$B_{\rm DIM}({\rm cm}^{-1})^{\rm f}$	0.083 <sup>i</sup>		
Vibrational frequ	encies in cm <sup>-1</sup> .	<sup>h</sup> Reference 23.	
<sup>b</sup> Rotational consta	ints in $cm^{-1}$ .	<sup>i</sup> Reference 9.	
<sup>c</sup> Polarizability in Å <sup>3</sup> .		<sup>j</sup> Reference 26.	
<sup>d</sup> Reduced mass in amu.		<sup>k</sup> Reference 21.	
<sup>e</sup> Dissociation energy in eV.		<sup>1</sup> Reference 24.	
<sup>f</sup> Rotational constant of dimer in cm <sup>-1</sup> .		<sup>m</sup> Reference 25.	
Reference 6.			

from the literature. $^{6,9,21,23}$  For those that were not available, reasonable estimates were made. $^{24-26}$ 

The results of the phase space theory calculations are summarized in Figs. 3 and 6. In Fig. 6 the calculated distribution for a wavelength of 514 nm is compared with the measured product relative kinetic energy distribution. The agreement between the measured and calculated distributions is rather poor: the calculated distribution is substantially broader than the measured one. Similar results were obtained at the other wavelengths studied. In Fig. 3 the average kinetic energies are plotted. The points are the experimental data and the dashed line labeled  $\tilde{X}$  is the phase space theory calculation. The calculated average kinetic energies are substantially larger than the measured values and increase more rapidly with the available energy.

Both lasers have narrow bandwidths ( $\sim 6$  MHz for the ion laser and 40 GHz for the dye laser) so the use of a thermal J distribution in the calculations is questionable if a bound to bound transition is involved. However, the effects of the laser's narrow bandwidth will be to some extent washed out owing to the large number of populated low frequency vibrational modes in the ground state. Furthermore, calculations as a function of J showed that the total angular momentum had only a minor effect on the shape of the product relative kinetic energy distribution. Angular momentum cannot account for the discrepancy between the measured and calculated distributions.

The use of statistical phase space theory to predict product energy distributions is valid when the dissociation rate is controlled by the loose orbiting transition state (located at the centrifugal barrier). When the rate is controlled by a tight transition state at smaller r the use of statistical phase space theory is only valid if after passing through the tight transition state the trajectories remain statistical up to the orbiting transition state.<sup>27</sup> The association reaction between SO<sub>2</sub><sup>+</sup> and SO<sub>2</sub> proceeds at thermal energies so there is no significant activation barrier along the reaction coordinate. The loose orbiting transition state will control the rate of the



FIG. 6. Product relative kinetic energy distributions for the photodissociation of  $SO_2 \cdot SO_2^+$  at 514 nm. The points are the experimental data and the line the result of statistical phase space theory calculations (see the text).

forward asociation reaction and by microscopic reversability also the reverse dissociation of  $SO_2 \cdot SO_2^+$ . Phase space theory would thus be expected to predict the product energy distributions for this system quite well. However, for visible wavelength photodissociation of  $SO_2 \cdot SO_2^+$  dissociation occurs at energies substantially above the ground state dissociation threshold. As will be discussed in more detail below, at these high energies the orbiting transition state may not control the rate, i.e., transition state switching<sup>27,28</sup> may occur and the rate may be controlled by a tight transition state. A tight transition state is expected to occur between the orbiting transition state and unimolecular reactant even for systems without an activation barrier,<sup>28</sup> although this issue is currently a point of substantial discussion.<sup>29</sup>

As mentioned above, if a tight transition state controls the dissociation rate the use of statistical phase space theory to predict the product energy distributions is still valid if the trajectories remain statistical up to the orbiting transition state. The picture that has been emerging over the past few years is that statistical phase space theory works fairly well at low energies but underestimates the product relative kinetic energies at higher energies above the dissociation threshold.<sup>22,27–29</sup> This has been attributed to the bottleneck at the orbiting transition state "opening up" so that trajectories from the tight to the orbiting transition state become more direct and less statistical.<sup>27</sup> However, for SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> photodissociation statistical phase space theory overestimates the product relative kinetic energies.

A reasonable explanation for the discrepancy between the predictions of phase space theory and the experimental results is that the products are not produced in their ground electronic states, i.e., dissociation from the excited electronic state occurs more rapidly than internal conversion to the ground state. The results of phase space calculations assuming that the SO<sub>2</sub><sup>+</sup> product is in the  $\tilde{A}^2 A_2$  state and in the  $\tilde{B}^{2}B_{2}$  state are shown in Fig. 2 as the lines labeled  $\tilde{A}$  and  $\tilde{B}$ . These calculations are in much better agreement with the measured average relative kinetic energies. However, the calculated average relative kinetic energies still increase more rapidly with the available energy than the measured averages. A possible explanation for this could be that with the smaller photon energies the rate of internal conversion to the ground state is comparable to the rate of vibrational predissociation from the excited state. Thus significant amounts of ground state products are formed with larger kinetic energies than the excited state products. With larger photon energies the rate of vibrational predissociation from the excited state increases and becomes larger than the rate of internal conversion. Thus dissociation occurs mainly from the excited state to generate excited state products. Based on the information given in Fig. 3 and assuming that the excited state involved is the B state it is possible to make a crude estimate of the fraction which internally converts to the ground state. We obtain values of 4% at 458 nm and 44% at 590 nm for this fraction.

We will now consider the implications of the product angular distributions. As noted above the photoproduct angular distribution has the general form<sup>11,16</sup>

$$P(\theta) = (4\pi)^{-1} [1 + \beta(U) P_2(\cos \theta)],$$
(15)

in which  $\beta$ , the asymmetry parameter, can have values between +2 and -1. For  $\beta = 0$  the angular distribution is isotropic. The asymmetry parameter is a complex quantity. Its value depends on the angle between the transition dipole moment and the axis along which the products separate, and also on the lifetime of the excited molecule. If the lifetime is longer than a rotational period, the anisotropy of the product angular distributions is reduced. However, even with complete rotational averaging the photoproduct angular distribution will not, in general, be isotropic.<sup>30</sup> The extent to which complete rotational averaging reduces the anisotropy of the photoproduct angular distribution depends on the shape of the molecule.<sup>13</sup> The SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> cluster, with a structure of two loosely bound SO<sub>2</sub> moeties, is probably a near prolate spheriod for which complete rotational averaging will reduce the anisotropy by around 0.17.<sup>13</sup> Thus values of  $\beta$ outside the range  $0.34 > \beta > -0.17$  indicate that complete rotational averaging has not occurred. It is evident from Fig. 4 that for the larger fragment velocities and larger photon energies the value of the asymmetry parameter is greater than 0.34. This indicates that complete rotational averaging has not occurred at least for some of the products. The average rotational period is given by

$$\tau_r = \left(\frac{1}{2\pi}\sqrt{\frac{kT}{I}}\right)^{-1},\tag{16}$$

where I is the average moment of inertia. For  $SO_2 \cdot SO_2^+$  the average rotational period is around  $5 \times 10^{-12}$  s at 300 K.

From statistical reaction rate theory,

$$k(E) = \int_0^\infty dJ P(J) \frac{F(E,J)}{\rho(E,J)}, \qquad (17)$$

where F(E,J) is the flux through the transition state,  $\rho(E,J)$  is the density of states in the reactant, and P(J) is the reactant angular momentum distribution function. Calculations using this equation and the orbiting transition state lead to unimolecular rate constants in the range  $10^{16}-10^{17} \text{ s}^{-1}$  in the relevant energy range. These are obviously unrealistically large rate constants. However, they serve to demonstrate two important facts. First, that transition state switching<sup>27,29</sup> must be occurring and as a consequence in this energy range the rate of dissociation is controlled by a tight transition state; and second we are operating in an energy range where the rate of unimolecular dissociation could be comparable to a rotational period.

That the value of the asymmetry parameter increases with the product velocity relative to the center of mass is evident from Fig. 4. Does this indicate that reactant ions with a shorter lifetime result in products with larger relative kinetic energies? To answer this question we have to determine if there is a dynamical reason why the asymmetry parameter should change with fragment velocity. Even if complete rotational averaging occurs the asymmetry parameter still depends on the angle between the transition dipole moment and the axis along which the products recoil. Thus the asymmetry parameter can be written as

$$\beta = 2\langle P_2(\cos\gamma)\rangle D(b), \qquad (18)$$

in the limit of complete rotational averaging. In this equation,  $\gamma$  is the angle between the transition dipole moment and the dissociation axis, and  $\langle P_2(\cos \gamma) \rangle$  is the second degree Legendre polynomial averaged over the appropriate distribution functions. D(b) in Eq. (18) is the reduction in the anisotropy of the product angular distribution due to complete rotational averaging. D(b) depends on the molecular shape;  $b = I_z/I - 1$  where  $I_z$  is the moment of inertia about the symmetry axis and I is the moment of inertia about the axes perpendicular to the symmetry axis. Values for D(b) have been tabulated by Yang and Bersohn.<sup>13</sup>

We will now develop a simple statistical phase space model for  $\langle P_2(\cos \gamma) \rangle$ . If we assume that the transition dipole moment lies along the SO<sub>2</sub>-SO<sub>2</sub><sup>+</sup> axis in the cluster and that the long range SO<sub>2</sub>-SO<sub>2</sub><sup>+</sup> potential can be represented by the ion-induced dipole potential:

$$V(r) = -\frac{\alpha q^2}{2r^4} + \frac{L^2 \tilde{n}^2}{2\mu r^2},$$
 (19)

then  $\gamma$  can be evaluated by a straightforward trajectory calculation as illustrated in Fig. 7. To a good approximation  $\gamma$ depends only on the reduced orbital angular momentum  $L/L^*$ , where  $L^*$  is the maximum orbital angular momentum allowed for products with relative kinetic energy  $E_i$ . In Fig. 8(a),  $\gamma$  is plotted against  $L/L^*$ . For small values of  $L/L^*$ ,  $\gamma$  is small and for values of  $L/L^*$  near 1,  $\gamma$  approaches 80°.  $P_2(\cos \gamma)$  must now be averaged over the available phase space for products with total energy  $E_i$  total angular momentum J, and relative kinetic energy  $E_i$ :

 $\langle P_2(\cos \gamma) \rangle_L$ 

$$=\frac{\int dE_r \rho_v (E-E_t-E_r) \int \int dL \, dJ_r \, \rho_r (E_r, J_r) P_2(\cos \gamma)}{\int dE_r \, \rho_v (E-E_t-E_r) \int \int dL \, dJ_r \, \rho_r (E_r, J_r)},$$
(20)

in which all parameters have been defined above. Finally  $\langle P_2(\cos \gamma) \rangle_L$  must be averaged over the total angular momentum distribution function:

$$\langle P_2(\cos\gamma)\rangle_{L,J} = \int dJ P(J) \langle P_2(\cos\gamma)\rangle_L.$$
 (21)

The values of  $\beta$  obtained using this statistical phase space model are shown plotted in Fig. 4 as the dashed lines. The calculated values of  $\beta$  increase as the center of mass velocity increases but the increase is not as large as observed experimentally.

The origin of this increase in the calculated value of  $\beta$  can be understood by reference to Figs. 8(b) and 8(c). These



FIG. 7. Diagram illustrating the evaluation of the angle  $\gamma$  (see the text).

figures show the available  $L - J_r$ , phase space for a typical rotational plus kinetic energy of 0.5 eV and an average thermal value of the total angular momentum. The  $L - J_r$ , diagrams<sup>31</sup> are simply a statement of conservation of angular momentum:

$$L = J + J_r, ..., |J - J_r|,$$
(22)

$$J_r = J + L_{,...,} |J - L|, \qquad (23)$$

with energetic constraints (i.e., maximum L and  $J_r$  possible from energetic considerations):

$$J_r^* = (E_r/B_r)^{1/2}, \tag{24}$$

$$L^* = (E,\lambda)^{1/4},$$
 (25)

in which  $B_r$  is the reduced rotational constant of the products and  $\lambda$  is given by  $8\alpha q^2/\hbar^4$ . The shaded areas in Figs. 8(b) and 8(c) show the allowed values of L and  $J_r$ . A more detailed discussion of these types of diagrams is given in Ref. 31. For a fragment velocity of 200 ms<sup>-1</sup> relative to the c.m. [Fig. 8(b)] all values of L up to L \* are accessible. Referring to Fig. 8(a), larger values of L/L \* result in larger values of  $\gamma$ which will lead to a smaller value for  $P_2(\cos \gamma)$  and hence a



FIG. 8. Diagrams relevant to the phase space theory calculation of the asymmetry parameter  $\beta$  assuming complete rotational averaging (see the text). (a) shows a plot of the angle  $\gamma$  against the reduced orbital angular momentum  $L/L^*$ . (b) and (c) show the available  $L - J_r$ , phase space for the SO<sub>2</sub>/SO<sub>2</sub><sup>+</sup> system with a kinetic plus rotational energy of 0.5 eV (balance in vibration). The available  $L - J_r$ , phase space (shaded region) is shown for a product relative velocity of 200 ms<sup>-1</sup> in (b) and 800 ms<sup>-1</sup> in (c).

smaller value for  $\beta$ . For a fragment velocity of 800 ms<sup>-1</sup> the allowed values of L are restricted to be significantly less than  $L^*$  by the energetic constraint on  $J_r$ . This results in a larger value for  $\beta$ . Thus as shown in Fig. 4 the calculated value of  $\beta$  increases with the product center of mass velocity.

Calculated values for  $\beta$  are shown in Fig. 4 for two wavelengths 590 and 458 nm. The calculated values for  $\beta$  are slightly larger for 590 nm than for 458 nm. Note that the reverse trend is observed experimentally: the value of  $\beta$  is larger for smaller wavelengths. The origin of the change in the calculated values for  $\beta$  can be understood by reference to Fig. 8. For larger wavelengths, the available energy is smaller and this effectively results in the  $J^*$  limit sliding over towards the left, constraining L to smaller values and hence leading to larger values for  $\beta$ .

The calculations presented above demonstrate that even with complete rotational averaging and if dissociation occurs by a statistical unimolecular reaction the asymmetry parameter  $\beta$  is expected to vary with the product velocity relative to the c.m. The origin of this variation is conservation restrictions on the available angular momentum  $(L-J_r)$  phase space. The variation of  $\beta$  with velocity predicted by the statistical phase space theory model are somewhat smaller than observed experimentally. Larger discrepancies are observed for smaller wavelengths (458 and 488 nm). The agreement between the predictions of the model and the experimental data for the larger wavelengths (particularly 590 nm, but also 514 nm) is quite reasonable. As noted above the values of  $\beta$  at the higher velocity end of the smaller wavelength data are larger than 0.34 which indicates that complete rotational averaging has not occurred. If complete rotational averaging has not occurred then the model and Eq. (18) are no longer valid. Under these circumstances modeling the asymmetry parameter becomes significantly more difficult. The two terms in Eq. (18) become coupled and the lifetime must also be considered.

The observed changes in  $\beta$  with wavelengths are probably mainly due to changes in the lifetime of the SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> cluster. The results suggest that the lifetime increases as the wavelength is increased (smaller photon energies). From the published work of Yang and Bersohn<sup>13</sup> a time corresponding to five times the average rotational period emerges as a useful operational definition of complete rotational averaging. The experimental data for a wavelength of 590 nm seems consistent with complete rotational averaging, which would indicate a lifetime of  $> 2.5 \times 10^{-11}$  s. For a wavelength of 458 nm complete rotational averaging has not occurred. Based on the work of Yang and Bersohn<sup>13</sup> we make a rough estimate of the average lifetime as equal to a rotational period  $5 \times 10^{-12}$  s at 458 nm.

#### **V. CONCLUSIONS**

Briefly summarized, our main observations are:

(1) the shape of the product relative kinetic energy distributions are characteristic of statistical energy disposal. However, statistical phase space theory calculations (assuming the products are formed in their ground electronic states) substantially overestimate the fraction of the available energy partitioned into relative kinetic energy suggesting sub-



FIG. 9. Schematic potential energy diagram showing the proposed mechanism of photodissociation. VP = vibrational predissociation and IC = internal conversion.

stantial population of electronically excited  $SO_2^+$  products.

(2) The product angular distributions suggest that at 458 nm the lifetime is approximately one rotational period and at 590 nm the data indicates that the lifetime increases to >5 rotational periods.

The simplest interpretation of the data presented in this paper is shown schematically in Fig. 9. The absorption is from the ground state of the  $SO_2 \cdot SO_2^+$  cluster to highly vibrationally excited quasibound levels of a bound excited state. The bound excited state arises from one of the low lying excited states of  $SO_2^+$ . Dissociation occurs by vibrational predissociation (statistical unimolecular reaction) which would be expected to result in statistical energy disposal in the products. As we have already proposed above, at 458 nm dissociation occurs rapidly from the bound excited state but at 590 nm the rate of vibrational predissociation from the bound excited state is slower and internal conversion to the ground state competes with dissociation. At 590 nm the rate of internal conversion and the rate of direct dissociation are probably approximately the same. Using the lifetime data we can obtain an order of magnitude estimate for the rate of internal conversion as  $<4\times10^{10}$  s<sup>-1</sup> at 590 nm. Incidently, the failure to observe the other energetically accessible products (SO<sup>+</sup> + SO<sub>3</sub> and SO<sub>3</sub><sup>+</sup> + SO) from the photodissociation of SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> suggests that substantial activation barriers exist along the potential surface from the  $SO_2 \cdot SO_2^+$  cluster to these products.

Compared to the other dimer ions we have studied, e.g., NO·NO<sup>+</sup>, <sup>3</sup> N<sub>2</sub>·N<sub>2</sub><sup>+</sup>, <sup>4</sup> and CO<sub>2</sub>·CO<sub>2</sub><sup>+</sup>, <sup>5</sup> the SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> dimer ion is unique. The reason for this, as discussed in the Introduction, is that for NO·NO<sup>+</sup>, N<sub>2</sub>·N<sub>2</sub><sup>+</sup> and possibly CO<sub>2</sub>·CO<sub>2</sub><sup>+</sup>, the only excited states accessible in the visible wavelength range are repulsive states which correlate to ground state products. SO<sub>2</sub><sup>+</sup>, on the other hand, has several low lying excited electronic states. Thus, SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> has several excited states accessible that correlate to excited state products. One or more of these states may be bound and our experimental results suggest that photodissociation of SO<sub>2</sub>·SO<sub>2</sub><sup>+</sup> involves a transition to one of these low lying bound excited states.

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