

FIG. 2. Force measured between a silver surface and a mica surface in conductivity water (open circles) and in 10^{-4} M Na_2CO_3 (squares). The long-range interaction appears to be a double-layer repulsion with Debye lengths of 74 nm in water (corresponding to 1.7×10^{-5} M 1:1 electrolyte) and 20 nm in Na_2CO_3 (corresponding to 9×10^{-5} M, in good agreement with the nominal concentration). At short range a van der Waals-like attraction is apparent in water and there is a locally adhesive minimum at contact (indicated by the horizontal arrow). In Na_2CO_3 the interaction becomes steeply repulsive at 7 nm (vertical arrow).

but the silver must be negatively charged like the mica for a repulsion of the measured magnitude to be present. The change in the short-range force on addition of Na_2CO_3 to 10^{-4} M must be due to a change in conditions at the silver

surface—with two mica surfaces a van der Waals-like attraction is found in 10^{-4} M.¹⁸

Accurate measurements of surface forces between a silver surface and a mica surface can be made in liquids but any complications from surface roughness may be more serious when *two* such surfaces are allowed to interact. This may be especially true for the short-range solvation forces, whereas the long-range double-layer interaction may not be significantly influenced, as seems to be the case for two platinum surfaces in water.¹⁰ We are currently embarking on investigations of the interaction of two silver surfaces.

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On the photodetachment of $(\text{SO}_2)_2^-$

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Thermochemical measurements have provided a wealth of information on stepwise ion-solvation enthalpies in the gas phase.¹ High pressure mass spectrometric studies by Castleman² have established a ΔH of -1.04 eV for the process $\text{SO}_2^- + \text{SO}_2 \rightarrow (\text{SO}_2)_2^-$. Other studies by Castleman³ have found the enthalpy of dimerization for neutral sulfur dioxide to be -0.19 eV. By combining these values together with the adiabatic electron affinity of SO_2 (1.107 eV),⁴ the electron affinity of $(\text{SO}_2)_2$ can be calculated from a thermochemical cycle to be 1.96 ± 0.03 eV. In addition, a comparable value (1.9 eV) was also obtained by Herschbach⁵ via collisional charge transfer experiments. Other pertinent

work on $(\text{SO}_2)_2^-$ includes photodestruction cross section measurements by Vanderhoff,⁶ photodissociation and collision induced dissociation investigations by Bowers,⁷ and photodissociation studies by Castleman.⁸ The Bowers study suggests that $(\text{SO}_2)_2^-$ is composed of two SO_2 moieties which resonantly share the excess electron.

Over the past few years we have initiated a program to study the photoelectron (photodetachment) spectra of negative cluster ions.⁹⁻¹¹ Here, we report the results of a photoelectron study on $(\text{SO}_2)_2^-$ using visible photons. This represents our first opportunity thus far to compare the energetic implications of thermochemical and charge transfer experi-

ments on negative cluster ions with those from negative ion photoelectron spectroscopy.

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency laser beam, and energy analyzing the resultant photodetached electrons. Our apparatus has been described previously.¹² In this work, $(\text{SO}_2)_2^-$ ions were generated from sulfur dioxide in a supersonic expansion ion source similar to that developed by Haberland.¹³ A typical mass spectrum, showing ions of the $(\text{SO}_2)_n^-$ homologous series, is presented in Fig. 1.

Because of the relatively high electron affinity of $(\text{SO}_2)_2^-$ and the fact that we are presently limited to the use of visible photons, our photoelectron spectrum exhibits only the lower energy photodetachment transitions of $(\text{SO}_2)_2^-$. While this is a limitation, it does not prevent us from comparing the most important energetic implications of thermochemical, charge transfer, and photoelectron studies for this particular negative cluster ion. The photoelectron spectra of SO_2^- and $(\text{SO}_2)_2^-$, which we recorded with 2.540 eV photons, are presented in Fig. 2 on aligned center-of-mass electron kinetic energy scales. The photoelectron spectrum of SO_2^- is well known and is presented here for comparison. Too little of the $(\text{SO}_2)_2^-$ spectrum is seen to tell whether or not it is structured. Also, even though only a limited range scan is shown for $(\text{SO}_2)_2^-$ in Fig. 2, a full range scan to higher electron energies found no other spectral features. The sharp decrease in the number of electron counts on the low electron kinetic energy side of the $(\text{SO}_2)_2^-$ spectrum is an instrumental artifact which is due to the unavoidable decrease in the transmission functions of electron energy analyzers at low electron energies. Spectra that we recorded with 2.707 eV photons confirm that the photodetachment cross section of

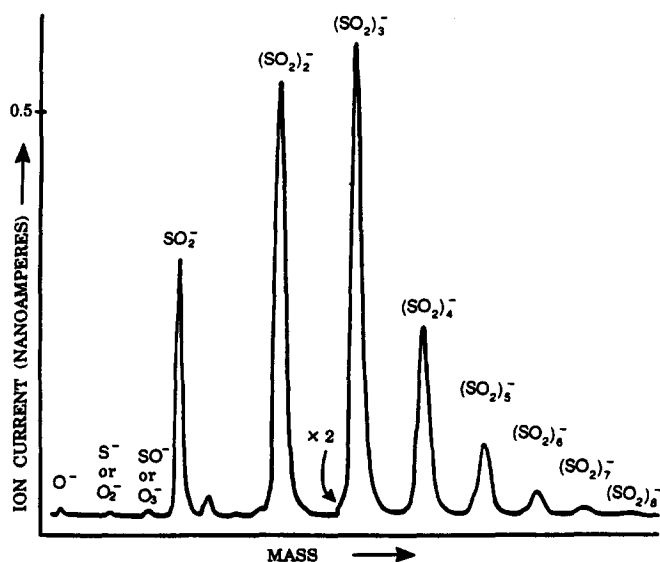


FIG. 1. A typical mass spectrum showing the negative ions generated by the nozzle-ion source with 2–3 atm of SO_2 (neat) behind a $\sim 20 \mu\text{m}$ diameter glass nozzle. Other operating parameters included: a nozzle temperature of 0°C , a beam energy of 500 eV, a filament bias relative to the nozzle of -185 V , and an emission current of 10 mA. The ion currents were measured in a Faraday cup beyond the ion-photon interaction region.

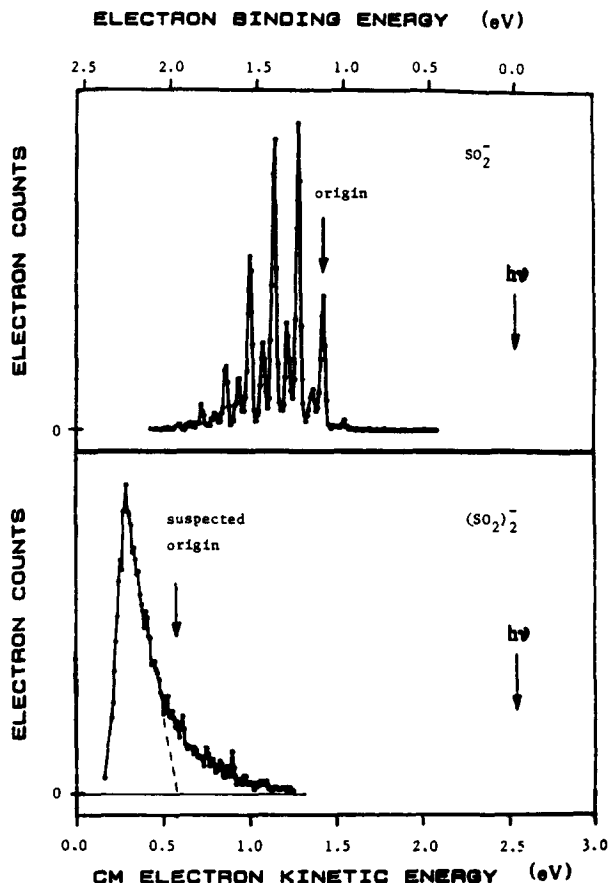


FIG. 2. The negative ion photoelectron spectra of SO_2^- and $(\text{SO}_2)_2^-$ both presented on the same center-of-mass electron kinetic energy scale for comparison. The $(\text{SO}_2)_2^-$ spectrum was recorded over 1 h with $5 \times 10^{-10} \text{ A}$ of $(\text{SO}_2)_2^-$, with a channel spacing of 0.0085 eV, and with 150 circulating Watts of 4880 Å laser power. The instrumental resolution of the electron energy analyzer was 30 meV. The dashed line shows the extrapolation to the transition origin.

$(\text{SO}_2)_2^-$ is still increasing at the false maximum in the 2.540 eV spectrum.

Assuming relatively small contributions from hot-band transitions, the origin transition in the $(\text{SO}_2)_2^-$ spectrum should reside along its high electron kinetic energy side. This portion of the spectrum is most probably comprised of an unresolved vibrational progression which terminates at the origin transition and a more gently sloping, higher electron energy tail due to whatever hot-band contributions are present. Extrapolation of the steepest sloping linear portion of this leading edge to zero electron counts (see Fig. 2) suggests that the origin transition occurs at an electron energy of $0.6 \pm 0.2 \text{ eV}$. This corresponds to an electron binding energy of $1.9 \pm 0.2 \text{ eV}$, and is thus consistent with the electron affinity values implied by both thermochemical and charge transfer studies. A comparison with the measured thermochemical quantities can also be made by considering the spectral shifts exhibited in Fig. 2. The energy difference between the origin of the SO_2^- spectrum and the suspected origin of the $(\text{SO}_2)_2^-$ spectrum implies that the excess electron on $(\text{SO}_2)_2^-$ is stabilized with respect to that on SO_2^- by roughly 0.8 eV. This viewpoint is consistent with the thermochemical results because it implies

$$EA[(\text{SO}_2)_2] - EA[\text{SO}_2]$$

$$= D[\text{SO}_2^- \cdots \text{SO}_2] - D[\text{SO}_2 \cdots \text{SO}_2] = \sim 0.8 \text{ eV},$$

where $EA[]$ denotes the electron affinities of the dimer and the monomer, and $D[]$ denotes the dissociation energies of the ionic and the neutral dimers into the indicated products.

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COMMENTS

Comment on: "Water-water and water-ion potential functions including terms for many-body effects," T. P. Lybrand and P. Kollman, *J. Chem. Phys.* **83, 2923 (1985), and on "Calculation of free energy changes in ion-water clusters using nonadditive potentials and the Monte Carlo method," P. Cieplak, T. P. Lybrand, and P. Kollman, *J. Chem. Phys.* **86**, 6393 (1987)**

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In a recent series of papers¹ the interaction energy of an assembly of water molecules and ions is computed taking into account many-body polarization effects. It is assumed that the system consists of point polarizable centers and charges. Each charge then induces dipoles on the polarizable spheres which contribute to the electrostatic energy. In the above papers this polarization energy is taken to be

$$E_{\text{pol}} = -\frac{1}{2} \sum_j \alpha_j \mathbf{E}_j \cdot \mathbf{E}_j, \quad (1)$$

where \mathbf{E}_j is the total electric field at site j :

$$\mathbf{E}_j = \mathbf{E}_j^{(0)} + \sum_k \mathbf{T}_{jk} \cdot \alpha_k \mathbf{E}_k, \quad (2)$$

where the term with the superscript (0) represents the electric field at the site j arising from all of the unscreened charges; that is, the unscreened Coulomb field and the sec-

ond term on the right-hand side represents the part of the electric field at site j due to all of the induced dipoles at other sites. The tensor \mathbf{T} is the standard dipole propagator.

Unfortunately, Eq. (1) is incorrect. The correct polarization energy is²

$$E_{\text{pol}} = -\frac{1}{2} \sum_j \alpha_j \mathbf{E}_j \cdot \mathbf{E}_j^{(0)}. \quad (3)$$

The difference between Eq. (1) used by Kollman *et al.*¹ and the correct expression given by Eq. (3) is that the larger unscreened Coulomb field appears in the last position instead of the total field. Equation (1) will give incorrect predictions of the solubility, and solvent structure around ions as well as the interaction between water molecules.

It should be recognized that Eq. (1) is simply wrong and should never be interpreted as arising from a "different physical model." Equation (3) is the correct equation for

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