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## Electric dipole moment of $\text{KrSO}_3$ <sup>a)</sup>

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(Received 6 October 1980; accepted 9 December 1980)

In a recent study,<sup>1</sup> we determined by molecular beam electric resonance spectroscopy the dipole moments and molecular symmetry of the weakly bound complexes  $\text{ArSO}_3$  and  $\text{N}_2\text{SO}_3$ . Both of these species were found to have a symmetric top structure in which the Ar atom or  $\text{N}_2$  molecule adds along the symmetry axis of the  $\text{SO}_3$ . Analysis of the radio frequency (Stark) spectra showed the dipole moments to be  $0.2676(3)D$  and  $0.46(1)D$  for  $\text{ArSO}_3$  and  $\text{N}_2\text{SO}_3$ , respectively.

Here we report the radio frequency spectrum of  $^{84}\text{KrSO}_3$ . A beam of this complex was produced by expanding a mixture of Ar, Kr, and  $\text{SO}_3$  at 900 Torr through a 3 m nozzle at 25 °C. The mixture was produced by pulse-injecting<sup>2</sup> pure Kr into a flowing stream of Ar seeded with  $\text{SO}_3$ . This technique provides a convenient method of controlling the concentration of Kr in the mixture during the experiment. The concentration of Kr was approximately 10%; that of  $\text{SO}_3$  is more difficult to estimate.<sup>1</sup> Thirty percent of the straight through beam was focused around a movable beam obstacle by 20 kV on the quadrupolar A field. Spectra were taken monitoring the mass peak of the parent ion  $^{84}\text{Kr}^{32}\text{S}^{16}\text{O}_3^+$  ( $m/e = 164$ ) which contains the most abundant Kr, S, and O isotopes, and has zero nuclear spin as well.

The Stark spectrum of  $^{84}\text{KrSO}_3$  is extremely simple. Due to the absence of off-axis nuclear spin, only the  $K=0, 3, 6, \dots$  levels exist and the transitions  $\Delta M_J = \pm 1$  are easily assigned. Table I gives the measured transi-

tion frequencies and their assignments. The frequencies fit the normal first-order Stark effect for a symmetric top. The dipole moment obtained from these data is  $0.369(2)D$ . The more complete study of  $\text{ArSO}_3$  established a symmetric top structure. There is little reason to expect a profound structural difference in  $\text{KrSO}_3$ .

It is of interest to compare the Ar and Kr complexes of  $\text{SO}_3$  with those of  $\text{ClF}$ . Table II lists the induced dipole moment for these four systems. For both  $\text{SO}_3$  and  $\text{ClF}$ , the induced moment is greater for the Kr complex than for the Ar complex. For both Ar and Kr, the induced moment is greater for the  $\text{SO}_3$  complex than for the corresponding  $\text{ClF}$  complex. The ratio of polarizabilities of Kr and Ar is 1.51. Novick *et al.*<sup>4</sup> have pointed out that this is close to the ratio of induced electric dipole moments of  $\text{KrClF}$  and  $\text{ArClF}$ , namely,

TABLE I. Observed radio frequency transitions in  $\text{KrSO}_3$ .

Frequency (MHz)	$E$ (V/cm)	$J$	$K$
1.33 (3)	100.73	6	$\pm 3$
1.89 (3)	100.73	5	$\pm 3$
2.82 (3)	100.73	4	$\pm 3$
4.66 (3)	100.61	3	$\pm 3$

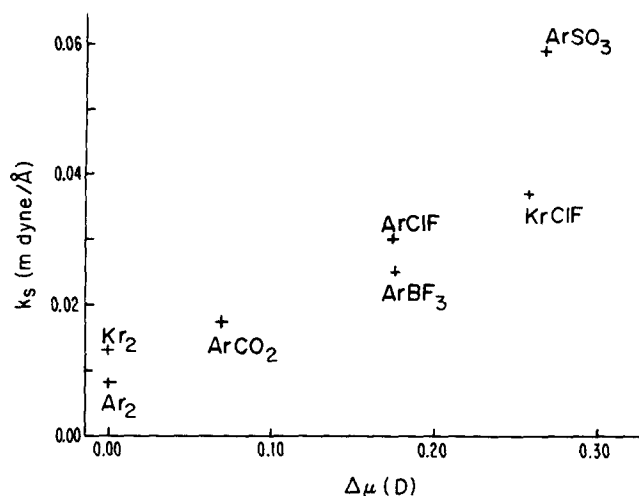


FIG. 1. Plot of induced dipole moment versus stretching force constant for some simple van der waals molecules.

1.47. The same ratio for  $\text{KrSO}_3$  and  $\text{ArSO}_3$  is 1.38, which is considerably lower than the ratio of polarizabilities of Kr and Ar.

The dipole moments of the  $\text{SO}_3$  complexes are essentially induced moments and as such likely reflect the strength of the intermolecular interactions involved. That the magnitude of the induced dipole moment correlates with binding strength can be seen by examining a plot of induced dipole moment versus force constants for a number of simple weakly bound complexes. Such a plot is shown in Fig. 1. It is seen that for pairs of complexes in which one moiety is the same, there is a general correlation between force constant and induced moment. It seems reasonable, therefore, to infer that  $\text{KrSO}_3$  is a stronger complex than  $\text{ArSO}_3$ . The out-of-plane bending deformation for the complexes  $\text{ArBF}_3$ ,<sup>5</sup>  $\text{N}_2\text{BF}_3$ ,<sup>5</sup>  $\text{COBF}_3$ ,<sup>5</sup> and  $\text{ArSO}_3$ <sup>1</sup> has been shown to be less than  $1^\circ$ , and there seems no reason to expect  $\text{N}_2\text{SO}_3$  or  $\text{KrSO}_3$  to be exceptions. For an S-O bond moment of  $1D$ , the contribution to the dipole moment of  $\text{SO}_3$  complexes would be about  $0.05D$ . Hence, the observed dipole moments are not explained in this manner.

The complexes of  $\text{SO}_3$  with Ar, Kr, and  $\text{N}_2$  have larger induced moments than any other complexes with these binding partners, including those of the strong Lewis acids  $\text{ClF}$  and  $\text{BF}_3$ . The ability of  $\text{SO}_3$  to strongly bind these substrates is probably due to its strength as a Lewis acid.

Complete structural information for  $\text{KrSO}_3$  is not presented in this work. There is likely sufficient information available, however, to estimate the Kr-S distance. The average rare gas-halogen distances in  $\text{ArClF}$  and  $\text{KrClF}$  are 3.330 and 3.388 Å, respectively, making the Kr-Cl distance longer by 0.058 Å. Using the Ar-S dis-

TABLE II. Comparison of the induced dipole moment for the Ar and Kr complexes of  $\text{SO}_3$  and  $\text{ClF}$ .

	$\Delta\mu (D)$		$\Delta\mu (D)$
$\text{ArSO}_3$ <sup>a</sup>	0.2676	$\text{ArClF}$ <sup>b</sup>	0.175
$\text{KrSO}_3$ <sup>c</sup>	0.369	$\text{KrClF}$ <sup>d</sup>	0.257

<sup>a</sup>Reference 1.

<sup>b</sup>Reference 3.

<sup>c</sup>This work.

<sup>d</sup>Reference 4.

tance in  $\text{ArSO}_3$  (3.35 Å) and assuming that  $R_{\text{Kr-X}}(\text{KrClF}) - R_{\text{Ar-X}}(\text{ArClF}) = R_{\text{Kr-S}}(\text{KrSO}_3) - R_{\text{Ar-S}}(\text{ArSO}_3)$ , we obtain a Kr-S distance of 3.41 Å. Interestingly, for the less strongly bound complexes of Ar and Kr with  $\text{HF}$ ,<sup>6</sup>  $\text{HCl}$ ,<sup>7</sup>  $\text{DCI}$ ,<sup>7</sup>  $\text{HBr}$ ,<sup>8</sup> and  $\text{DBr}$ ,<sup>8</sup> the Kr-X distances are longer than the Ar-X distances by 0.107, 0.105, 0.101, 0.111, and 0.099 Å, respectively. If the difference between Ar and Kr binding distances in hydrogen halide and  $\text{ClF}$  complexes is due to binding strength, then we might expect, in light of the relative induced moments for  $\text{ClF}$  and  $\text{SO}_3$  complexes, that  $R(\text{KrSO}_3) - R(\text{ArSO}_3) < R(\text{KrClF}) - R(\text{ArClF})$ . This would make 3.41 Å an upper bound to the Kr-S distance. A lower bound may be chosen as 3.35 Å, the  $\text{ArSO}_3$  weak bond length. Thus, by this reasoning, the Kr-S bond length is expected to be nominally  $3.38 \pm 0.03$  Å. Microwave studies to fully established the structure of  $\text{KrSO}_3$  were not pursued because of long term deleterious effects of  $\text{SO}_3$  on the apparatus.

<sup>a</sup>This work was supported by the National Science Foundation.

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