



FIG. 2. Product rotational state distribution for the desorbing H<sub>2</sub> molecule. (a)  $v=0$ ; (b)  $v=1$ ; (c)  $v=2$ ; (d)  $v=3$ . The locations of selected excited vibrational states ( $E_{v,j}$ ) are indicated.

(e) Statistical considerations tend to favor higher rotational states [due to the  $(2j+1)$  degeneracy]. How well are these results explained by statistical theories?

Several of these questions will be addressed in a more detailed presentation of this research to appear later. However, the preliminary results seem to

indicate that there exist interesting dynamical effects to be studied in heterogeneous chemical reactions.

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## Theoretical predictions of stable negative ions: HF<sup>-</sup>, LiH<sup>-</sup>, NaH<sup>-</sup>

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(Received 29 July 1975)

We have employed the equations-of-motion (EOM) method<sup>1,2</sup> to investigate the possible existence of stable (with respect to dissociation and autodetachment) states

of HF<sup>-</sup>, LiH<sup>-</sup>, and NaH<sup>-</sup>. The results lead us to predict that the lowest <sup>2</sup>Σ states of these anions are stable. These negative ions, which have one electron outside a

closed-shell parent whose dipole moment is greater than 1.625 D ( $\mu_{\text{HF}} = 1.82$  D,  $\mu_{\text{LiH}} = 5.88$  D,  $\mu_{\text{NaH}} = 6.98$  D) have not yet been detected experimentally as stable species. The absence of experimental observation of the above anions and theoretical work<sup>3</sup> showing that bound states exist for an electron in the field of a dipole of (*fixed*) magnitude greater than 1.625 D make it interesting and timely to consider the possibility that HF, LiH, and NaH can have stable negative ions.

In this investigation, we employed basis sets in which diffuse Slater-type orbitals (STO's) have been added to the electropositive atom to permit the "extra" electron to attach to the positive end of the polar parent molecule. Earlier attempts<sup>4</sup> to study the ground state of HF<sup>-</sup> have either excluded diffuse basis functions, assuming that they would allow the extra electron to escape, or have not included appropriate diffuse functions on the hydrogen atom. The basis sets used in our work are described below.

We find, even in the Koopmans' theorem<sup>5</sup> (KT) approximation; that HF<sup>-</sup>, LiH<sup>-</sup>, and NaH<sup>-</sup> are bound species with respect to autodetachment and dissociation. Corrections to the KT approximation arising from orbital relaxation and electron correlation effects are found to be small. This result suggests an interpretation in which the extra electron resides in a nonbonding orbital which permits little dynamic interaction with the other electrons. These results are discussed in detail later.

Displayed in Table I are the basis sets used in these calculations. They were constructed by taking dominant orbitals from the appropriate neutral-molecule bases of Cade and Huo<sup>6</sup> (CH) and adding optimized diffuse *s* and *p* orbitals on the more electropositive atom. In particular, the LiH basis contains ten of the most important CH STO's to which a diffuse 2*s* hydrogen orbital and two sets

TABLE I. STO basis sets for LiH, NaH, and HF. LiH:  $R_e = 3.015$  a.u.,  $E = -7.9866$  a.u.; NaH:  $R_e = 3.566$  a.u.,  $E = -161.9422$  a.u.; HF:  $R_e = 1.733$  a.u.,  $E = -100.0192$  a.u.

LiH		NaH		HF	
1s <sub>0</sub> Li	(4.6990)	1s <sub>0</sub> Na	(11.1543)	1s <sub>0</sub> F	(14.1095)
1s <sub>0</sub> 'Li	(2.5212)	2s <sub>0</sub> Na	(2.0006)	1s <sub>0</sub> 'F	(7.9437)
2s <sub>0</sub> Li <sup>a</sup>	(1.2000)	2p <sub>0</sub> Na	(4.1786)	2s <sub>0</sub> F	(3.2563)
2s <sub>0</sub> 'Li <sup>a</sup>	(0.7972)	2p <sub>0</sub> 'Na	(2.2798)	2s <sub>0</sub> 'F	(1.9346)
2s <sub>0</sub> ''Li <sup>a</sup>	(0.6000)	3s <sub>0</sub> Na	(6.2601)	2p <sub>0</sub> F	(4.2784)
2s <sub>0</sub> '''Li <sup>a</sup>	(0.3000)	3s <sub>0</sub> 'Na	(0.9106)	2p <sub>0</sub> 'F	(2.3732)
2p <sub>0</sub> Li	(2.7500)	3s <sub>0</sub> ''Na	(0.4000)	2p <sub>0</sub> ''F	(1.4070)
2p <sub>0</sub> 'Li	(1.2000)	3s <sub>0</sub> '''Na <sup>a</sup>	(0.2000)	2p <sub>0</sub> 'F	(4.2614)
2p <sub>0</sub> ''Li	(0.7369)	3p <sub>0</sub> Na	(1.2631)	2p <sub>0</sub> ''F	(2.3291)
2p <sub>0</sub> '''Li	(0.6000)	3p <sub>0</sub> 'Na	(0.7108)	2p <sub>0</sub> '''F	(1.3584)
2p <sub>0</sub> ''''Li <sup>a</sup>	(0.3000)	3p <sub>0</sub> ''Na <sup>a</sup>	(0.4000)	1s <sub>0</sub> H	(2.4605)
2p <sub>0</sub> 'Li	(0.7369)	3p <sub>0</sub> '''Na <sup>a</sup>	(0.1500)	1s <sub>0</sub> 'H <sup>a</sup>	(1.3727)
2p <sub>0</sub> ''Li	(0.3500)	2p <sub>0</sub> Na	(4.1742)	2s <sub>0</sub> H	(2.4615)
1s <sub>0</sub> H	(1.5657)	2p <sub>0</sub> 'Na	(2.2828)	2s <sub>0</sub> 'H <sup>a</sup>	(0.4000)
1s <sub>0</sub> 'H	(0.8877)	3p <sub>0</sub> Na	(0.9636)	2s <sub>0</sub> ''H <sup>a</sup>	(0.2000)
2s <sub>0</sub> H <sup>a</sup>	(0.4000)	1s <sub>0</sub> H	(0.7808)	2p <sub>0</sub> H <sup>a</sup>	(0.4000)
2p <sub>0</sub> H	(1.3765)	2s <sub>0</sub> H <sup>a</sup>	(0.4000)	2p <sub>0</sub> 'H <sup>a</sup>	(0.2000)

<sup>a</sup>Atomic orbitals important in the description of the LUMO.

TABLE II. Equations-of-motion electron affinities and ionization potentials and Koopmans' theorem estimates (eV).

Species	E. A. or I. P.	EOM	- $\epsilon_{\text{LUMO}}$	Exptl <sup>2</sup>
LiH	E. A.	0.2986	0.1997	...
NaH	E. A.	0.3618	0.2897	...
HF	E. A.	0.3558	0.3555	...
HF	I. P.	15.87	17.79	16.01
BH	I. P.	9.53	9.30	9.77
BeH <sup>-</sup>	I. P.	0.77	0.51	0.74
OH <sup>-</sup>	I. P.	1.76	3.06	1.825

of lithium  $\pi$  functions were added. Diffuse 2*s* and 2*p* $\sigma$  orbitals, two of each, were placed on the lithium nucleus to permit the formation of *s-p* hybrid orbitals. Exponents of the added functions were optimized at the experimental equilibrium bond length ( $R_e$ ) of LiH, after which EOM calculations were carried out for several internuclear distances.

The NaH basis was constructed in an analogous fashion from 15 dominant CH orbitals by adding a diffuse hydrogen 2*s* function and two diffuse 3*s* and 3*p* $\sigma$  orbitals on sodium. The exponents of these orbitals were optimized at the experimental  $R_e$  of NaH.

The basis for HF consists of 16 CH orbitals which are most important in the description of the neutral molecule to which we have added and optimized two diffuse 2*s* and 2*p* $\sigma$  orbitals on the hydrogen atom. For each of the three species, optimization of the exponents of the diffuse orbitals led to a *negative* orbital energy for the lowest unoccupied molecular orbital (LUMO). Thus, even in KT, the  $^2\Sigma$  states of the ions are stable at the equilibrium geometry of the parent.

The results of our EOM calculations and the KT estimates for the equilibrium bond length of the parent are shown in Table II. Also shown, for perspective, are results of earlier calculations reported in Ref. 2. Over a range of internuclear distances (2.0–4.5 a.u. for LiH, 2.0–4.25 a.u. for NaH, and 0.75–2.6 a.u. for HF), the anion potential curves lie below the neutral molecule curves.<sup>7</sup> Curve crossings did not occur, and the equilibrium bond lengths of the ions were nearly the same as those of the respective neutrals. The fact that differences between KT and EOM electron affinities are less than 0.1 eV is indicative of small correlation and relaxation effects in the electron attachment process. Small relaxation effects can be understood by recalling that the LUMO is a virtual Hartree-Fock orbital of the parent which has been calculated using the Coulomb and exchange potential of *all* the parent's electrons. The LUMO is thus appropriate for describing an electron in the field of the parent. The small correlation energy change is in accord with a description in which the extra electron resides in a region of space which is essentially unoccupied by other electrons. We have found (see Table I) that the LUMO's in these systems are nonbonding orbitals on the electropositive atoms. Thus, it is not surprising that formation of the negative ion does not give large relaxation or correlation effects nor does it significantly alter the equilibrium internuclear

separation.

In summary, we find that our EOM electron affinity results lead us to predict that LiH, NaH, and HF can bind an electron to form a stable anion. Our studies demonstrate that the inclusion of diffuse basis functions on the electropositive center is essential for obtaining stable states of HF<sup>-</sup>, LiH<sup>-</sup>, and NaH<sup>-</sup>. A more detailed description of our results will be reported in a full paper in the near future.

This research was supported by Grant DAH CO4-74-G-0221 from the U. S. Army Research Office at Durham. K. D. J. thanks A. Herzenberg, C. Lineberger, and G. J. Schulz.

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<sup>7</sup>Based upon our experience with the EOM method, we feel that the stabilities of the anions considered here are probably underestimated by 0.1–0.2 eV. We have never encountered a situation in which the EOM theory has overestimated the stability of a negative ion. The fact that all three ions are found to be stable in Koopmans' theorem is strong evidence that they are stable.

## The measurement of $T_1$ and $T_2$ for the ammonia inversion doublets in the ground vibrational state\*

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(Received 17 July 1975)

We report in this Communication the measurement of  $T_1$  and  $T_2$  in the ground vibrational state inversion levels of <sup>15</sup>NH<sub>3</sub> for several values of  $J$  and  $K$ . We use the newly developed transient experiments to measure, independently,  $T_1$  and  $T_2$ .

Earlier experimental data coming from power saturation measurements led to the conclusion that  $T_1 = T_2$  in the inversion doublets of NH<sub>3</sub>.<sup>1</sup> However, we find that the  $T_2/T_1$  ratio varies over the range  $1.0 \leq T_2/T_1 \leq 2$ , as shown in Table I.

We have earlier developed the theory and experimental verification for transient experiments in microwave spectroscopy.<sup>2–6</sup> According to this theory, when a two level quantum mechanical system is brought into resonance with a strong radiation field, a macroscopic polarization is induced and the population difference of the two levels can be driven from equilibrium. If the electromagnetic field is removed, the polarization decays with a characteristic relaxation time  $T_2$ , whereas the population difference returns to thermal equilibrium with a relaxation time  $T_1$ . The relaxation mechanism can be described by Bloch-type equations.

The  $T_2$  data reported in Table I for the inversion transitions in <sup>15</sup>NH<sub>3</sub> were measured by transient emission as a function of pressure using Stark switching of the energy levels as previously described.<sup>5</sup> The results for  $1/T_2$  in Table I agree well with those transitions measured

earlier.<sup>5</sup> We also found in this earlier work<sup>5</sup> that  $T_2$  is the same for the various  $M$  states within a given  $(J, K)$  level for the inversion doublets. We have used the <sup>15</sup>N isotopic form of NH<sub>3</sub> in these experiments to avoid the additional interpretive complications involving the nuclear quadrupole splittings in <sup>14</sup>NH<sub>3</sub>.

$T_1$  was measured by a  $\pi, \tau, \pi/2$  pulse sequence, a method that is also described earlier.<sup>6</sup> In this method the  $J = M$  level for a certain inversion doublet is brought into resonance with a strong microwave field by switching the Stark field on. After a time  $t_r$  the polarization oscillates back to zero. By this  $\pi$  pulse the population difference is nearly inverted. The Stark field is then switched off and the population decays exponentially back

TABLE I. The values of  $1/T_1$ ,  $1/T_2$ , and the  $T_2/T_1$  ratios for several  $(J, K)$  states in the ground vibrational state of <sup>15</sup>NH<sub>3</sub>. Single standard deviations are given.

$(J, K)$	$\frac{1}{T_1}$ (MHz/mTorr)	$\frac{1}{T_2}$ (MHz/mTorr)	$\frac{T_2}{T_1}$
(1, 1)	$0.20 \pm 0.01$	$0.141 \pm 0.003$	$1.4 \pm 0.1$
(2, 1)	$0.11 \pm 0.01$	$0.097 \pm 0.003$	$1.1 \pm 0.1$
(2, 2)	$0.22 \pm 0.01$	$0.155 \pm 0.003$	$1.4 \pm 0.1$
(3, 2)	$0.19 \pm 0.01$	$0.120 \pm 0.003$	$1.6 \pm 0.1$
(3, 3)	$0.28 \pm 0.02$	$0.157 \pm 0.003$	$1.8 \pm 0.2$
(4, 3)	$0.23 \pm 0.01$	$0.134 \pm 0.003$	$1.7 \pm 0.1$
(4, 4)	$0.29 \pm 0.02$	$0.157 \pm 0.003$	$1.8 \pm 0.2$