FIG. 1. UV fluorescence excitation spectrum observed upon positioning the pump laser on the maximum of the $Ne^{35}Cl_2$ $11 \leftarrow 0$, $B \leftarrow X$ band contour and scanning the probe laser energy through the $^{35}Cl_2$ $3 \leftarrow 10$, $E \leftarrow B$ band.

rotational state populations. Since we observe qualitatively similar results for the the $^{35}Cl^{37}Cl$ species, the intensity alternation is not primarily due to conservation of nuclear spin but does reflect the role of symmetry in the dissociation dynamics. Work in progress is exploring the dependence of the rotational product state distributions upon the prepared rotational state of the excited van der Waals molecule.

In summary, the dynamics of $NeCl_2$ is very different from those observed for He, Ne, and Ar bound to I_2 or He and Ne bound to ICl. All rotational product states allowed by energetic constraints are apparently populated which suggests that the predissociation mechanism is not a direct $V \rightarrow T,R$ process. The final even/odd rotational state quantum number distribution depends on the initially excited rovibronic level of the van der Waals complex.

a classical impact parameter of 7.2 Å. For a direct relaxation mechanism starting from the T-shaped $NeCl_2$ structure, which has a half-collision impact parameter of zero, one expects the rotational distribution to be sharply peaked near $j = 0$. We observe a rotational distribution that, while peaked at low j, has a relatively flat tail that extends from $j = 15$ to j_{max}. This phenomenon may suggest that in addition to the direct half collision mechanism there exists an indirect mechanism which involves preliminary relaxation of the Cl_2 to the "bending" van der Waals mode followed by rotational predissociation.

The vibrational predissociation mechanism is such that the even and odd j rotational states are not equally populated. Excitation at the bandhead of the van der Waals $B \leftarrow X$ feature leads to preferential population of even j rotational states. By tuning the excitation laser to different regions of the $NeCl_2$ $B \leftarrow X$ band contour the even/odd j Cl_2 rotational state population ratio is observed to change. When the excitation laser is tuned to the red wing of the band contour the odd j Cl_2 rotational states are nearly absent. The spectrum presented in Fig. 1 shows this even/odd alternation in

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Towards HF SCF value of electron affinity of SF₆

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After years of uncertainty,[1] the experimental value of the adiabatic electron affinity (aEA) of SF_6 seems to have been stabilized at 1.05 ± 0.1 eV.[2] So far, the most accurate HF SCF evaluation of aEA was done by Hay.[3] Using a fairly small basis set and considering only octahedral geometry he obtained aEA of 1.03 eV (without zero-point correction). This value is often quoted as the Hartree–Fock value of aEA.[4] However, it seems that this value, albeit very close to the experimental one, does not leave any room for effects due to (a) larger basis sets, (b) nonoctahedral geometries of the ion, and (c) correlation effects.

TABLE I. Total energies (in hartrees) of SF_6 ($^1A_{1g}$) and SF_6^- ($^2A_{1g}$).

$R(a_0)$	$E(SF_6)$	$E(SF_6^-)$
2.9	−994.189 55	−994.177 03
2.95	−994.194 69	−994.182 37
3.0	−994.191 97	−994.180 08
3.05	−994.182 61	−994.171 91
3.1	−994.167 68	−994.191 02
3.2	−994.124 69	−994.205 59
3.3	−994.069 10	−994.199 12
3.4	⋯	−994.176 86

TABLE II. Total energies (in hartrees) of SF_6 ($^1A_{1g}$) at 2.95 a_0 and SF_6^- ($^2A_{1g}$) at 3.20 a_0. Energy differences (in eV) are defined as: $\Delta E_1 = E(X) - E(A)$ for SF_6, $\Delta E_2 = E(X) - E(A)$ for SF_6^-, and $\Delta E = E(^1A_{1g};$ 2.95 $a_0) - E(^2A_{1g}; 3.20 a_0)$.

Basis	$SF_6(^1A_{1g})$	ΔE_1	$SF_6^- (^2A_{1g})$	ΔE_2	$\Delta E \approx aEA$
A	− 994.194 69	0.00	− 994.205 59	0.00	0.30
B	− 994.184 08	0.29	− 994.198 96	0.18	0.40
C	− 994.115 95	2.14	− 994.163 73	1.14	1.30
D	− 994.106 52	2.40	− 994.157 89	1.30	1.40
E	− 994.252 64	− 1.58	− 994.240 07	− 0.94	− 0.34

In an attempt towards evaluating the HF SCF value of aEA we used a large, contracted basis set. For sulfur [$5s5p3d$] basis with structure (93211/72111/411) was employed (containing diffuse functions for both Rydberg and anion states[5] together with d-type polarization function[6]). The exponents of five d-type functions contracted to (41) were obtained by fitting to the numerical HF $3d$ radial function of ^5D [Ar]$3s^23p^33d^1$. The basis set for fluorine was [$3s4p1d$] or (721/5111/1).[6] The basis sets were chosen for their ability to adequately approximate the atomic Hartree–Fock excitation energies and electron affinities. Cartesian GTFs were used in all the calculations.

The calculated potential energy curves in octahedral geometry, presented in Table I, give the following (interpolated) parameters at the equilibrium: for SF_6, internuclear distance $R_e = 1.565$ Å , total energy $E_e = - 994.194\ 78$ hartree, and the frequency of the symmetric stretch mode $\bar{\nu}_0 = 851$ cm^{-1}. For SF_6^-, $R_e = 1.704$ Å, $E_e = - 994.205\ 98$ hartree, and $\bar{\nu}_0 = 698$ cm^{-1}. The aEA, without zero-point correction, is only 0.30 eV. Comparison of the present results with those of Hay[3] indicates that even though the different basis sets used give similar equilibrium geometries the values of aEA are different.

To clarify the influence of basis sets on aEA we performed SCF calculations on $^1A_{1g}$ state of SF_6 at $R_{S-F} = 2.95$ a_0 and on $^2A_{1g}$ state of SF_6^- at $R_{S-F} = 3.20$ a_0 using the following basis sets derived from the original one (denoted here as A):

(1) $B = A - 3d$ orbital on sulfur,
(2) $C = A - $ polarization function on fluorine,
(3) $D = A - 3d$ orbital on sulfur—polarization function on fluorine,
(4) $E = A + f$-type function on sulfur ($\zeta_f = 0.62$, obtained via the overlap criterion[6]).

(The basis set D is similar to that of Hay.[3]) The internuclear distances chosen are close to the equilibrium distances and the energy differences $\Delta E = E(SF_6; 2.95\ a_0) - E(SF_6^-; 3.20\ a_0)$ should be reasonably close to aEA.

The results, collected in Table II indicate that the d-type functions on fluorine atoms strongly affect the value of ΔE. The role of the sulfur $3d$ orbital is less significant in determination of the SCF value of aEA. The most conspicuous

feature is the effect of the f-type function on sulfur. This function, which does not contribute directly to the singly occupied $6a_{1g}$ orbital, brings about reversal of stability of SF_6 and SF_6^-. The f-type functions may influence the geometries of both SF_6 and SF_6^-, so that ΔE may no longer be the adequate approximation to aEA. Furthermore, different values of the exponents may be needed for SF_6 and SF_6^-.

The vertical EA was reported by Hay[3] to be − 1.57 eV. The present value (at 2.95 a_0) is − 0.34 eV. However, inspection of composition of the $6a_{1g}$ orbital of SF_6^- reveals that it is the most diffuse functions (3s-type GTF with $\zeta = 0.011$) which contribute most. Thus the $^2A_{1g}$ state in this region seems to be a projection of a continuum of states of $SF_6 + e^-$ onto a discrete basis set used in the SCF calculations. To elucidate the nature of this state, we performed SCF calculation at $R_{S-F} = 2.95$ a_0 replacing $\zeta_{3s} = 0.011$ by $\zeta_{3s} = 0.004$. This decreased the separation between $^1A_{1g}$ and $^2A_{1g}$ states to 0.12 eV. It seems that one could bring the two states arbitrarily close by supplying sufficiently diffuse functions.

The present calculations indicate that the HF SCF value of aEA is far from being determined. Clearly, d-type functions on fluorine atoms are needed; the $3d$ orbital on sulfur may probably be omitted (however, it may prove important in correlation energy calculation); the role of f-type functions on sulfur needs to be clarified; and finally, nonoctahedral geometries of SF_6^- have to be investigated. Ultimately, inclusion of the electron correlation effects may be necessary in order to bring about agreement between theoretical and experimental values of aEA.

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