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Photoelectron spectrum of the Xe···HCl van der Waals molecule

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Ultraviolet photoelectron spectroscopy (UVPES) has been employed to obtain the potential energy curves of the ground and the excited ionic states of van der Waals molecules such as Xe_2.[1] Molecular clusters of noble gases[2] and $(H_2O)_n$[3] have also been examined by this technique. We considered it most worthwhile to investigate the UVPES of triatomic Xe···HCl with a long Xe···H distance.[4] This van der Waals molecule has been studied by infrared and other spectroscopies and has a dissociation energy of ~ 300 cm^{-1} [5,6] with the Xe···HCl configuration being more stable than the Xe···ClH configuration.[7] We briefly discuss the nature of the excited ionic states of Xe···HCl in this report.

UVPE spectra of Xe + HCl mixtures were recorded at varied stagnation pressures with a home-built double-chamber spectrometer (resolution, 50 meV) wherein the molecular beam of premixed Xe and HCl coming through a sonic nozzle (of 0.1 mm) was crossed by HeI radiation (584 Å). In Fig. 1 we show a typical spectrum obtained at a stagnation pressure of 116 Pa containing features (a through e) of the van der Waals molecule, not present in the spectrum when the Xe + HCl mixture was passed through an effusive nozzle (see inset of Fig. 1). Furthermore, features due to the first ionization of Xe_2[8] or HCl dimer[9] are absent in the spectrum of Xe···HCl. A simple molecular orbital scheme of Xe···HCl suggests the presence of four levels $\pi(1)$, $\sigma(2)$, $\pi(2)$, and $\sigma(1)$ in the order of increasing energy wherein the two levels designated by (1) essentially have HCl character and those designated by (2) have Xe character (Fig. 2). Upon ionization, the π levels would be expected to show spin–orbit splitting. We can readily assign features a and e in the spectrum to the $^2\Pi(1)$ and $^2\Sigma(1)$ states. Appearance of only five features in UVPE spectrum suggests that the spin–orbit splitting is significant only in the case of the $\Pi(2)$ level (Fig. 2). We assign features c and d in the spectrum to the $^2\Pi_{3/2}(2)$ and $^2\Pi_{1/2}(2)$ states, respectively. Feature b is assigned to the $^2\Sigma(2)$ state. In Table I we list the adiabatic and the vertical ionization energies of the different states.

We have calculated the dissociation energies of the different states from the equation $D = D_0 + IE_0 - IE_1$ where D and D_0 are the dissociation energies of the ionic and ground states, respectively. While IE_0 is the adiabatic ionization energy of the state to which the ionic state dissociates, IE_1 is that of the ionic state in question. The results are presented in Table I. We find that only bands a and e correspond to bound states. We could construct preliminary potential energy curves of the excited ionic states of Xe···HCl with the available data, but further studies would be necessary to obtain reliable curves.

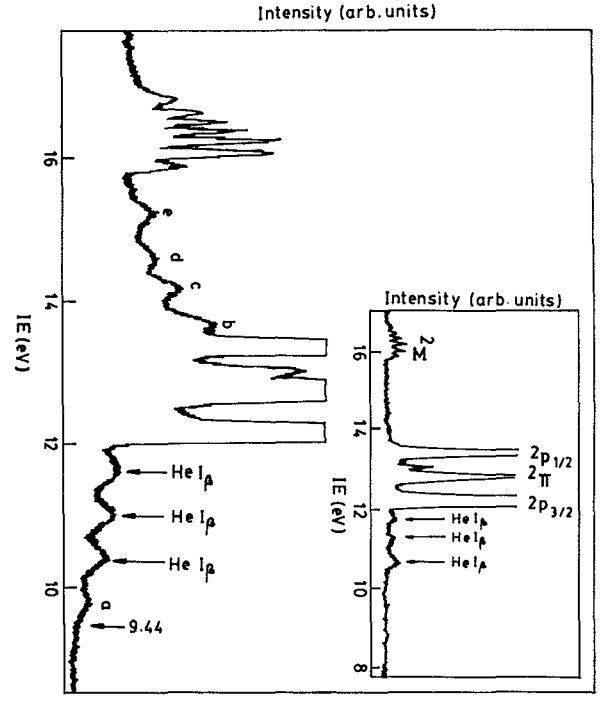

FIG. 1. UVPE spectrum of a Xe + HCl mixture recorded at a high stagnation pressure. Features a through e are due to the van der Waals molecule. He I_β features are also indicated. Inset shows the spectrum of Xe + HCl at a low stagnation pressure.

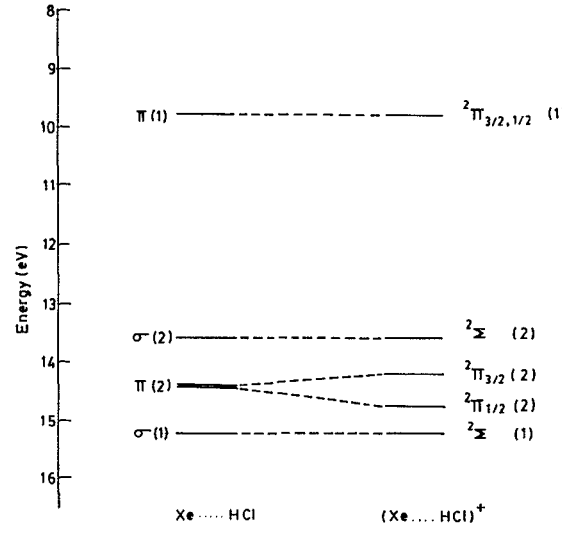

FIG. 2. Molecular orbital scheme for Xe···HCl in the ground and the ionic states.

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TABLE I. Ionization and dissociation energies for the different electronic states of Xe···HCl.

UVPES band	State[a]	Adiabatic IE(eV)[b]	Vertical IE(eV)	Dissociation energy(eV)
a	$^2\Pi_{3/2,1/2}(1)$	9.4	9.8	3.3
b	$^2\Sigma(2)$	13.6	13.7	...[c]
c	$^2\Pi_{3/2}(2)$	14.0	14.2	...[c]
d	$^2\Pi_{1/2}(2)$	14.5	14.7	...[c]
e	$^2\Sigma(1)$	15.0	15.3	1.3

[a] Suffixes (1) and (2) refer to states essentially derived from HCl and Xe, respectively.

[b] Adiabatic IEs of weakly interacting systems may not correspond to the minima of the potential energy surfaces when the ionic states are highly bound (Ref. 10). Large differences between the experimental and the theoretical values are not uncommon. The adiabatic IEs for the states a and e can therefore at best be the lowest estimates; the observed IEs are probably the result of transitions to excited vibrational states.

[c] Repulsive.

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[1] P. M. Dehmer and J. L. Dehmer, J. Chem. Phys. **68**, 3462 (1978).
[2] (a) F. Carnovale, J. B. Peel, R. G. Rothwell, J. Valldorf, and P. J. Kuntz, J. Chem. Phys. **90**, 1452 (1989). (b) E. D. Poliakoff, P. M. Dehmer, J. L. Dehmer, and R. Stockbaner, J. Chem. Phys. **75**, 1568 (1981).
[3] S. Tomoda, Y. Achiba, and K. Kimura, Chem. Phys. Lett. **87**, 197 (1982).
[4] J. S. Winn and W. Klemperer, J. Chem. Phys. **70**, 5157 (1979).
[5] J. M. Hutson and B. J. Howard, Mol. Phys. **45**, 769 (1982).
[6] E. W. Boom and J. van der Elsken, J. Chem. Phys. **77**, 625 (1982).
[7] M. Valegrakis and H. J. Loesch, Chem. Phys. **142**, 333 (1990).
[8] K. Norwood, G. Luo, and C. Y. Ng, J. Chem. Phys. **90**, 4689 (1989).
[9] R. D. Levin and S. G. Lais, *Ionization Potential and Appearance Potential Measurements, 1971–1981* (NSRDS–NBS 71, National Bureau of Standards, Washington D. C., 1982).
[10] T. Pradeep and C. N. R. Rao, J. Mol. Struc. **200**, 339 (1989).

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