

Studies on NaXe Clusters

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Abstract: The chemical shift of ²³Na in excimer NaXe was measured by using nuclear magnetic resonance (NMR) spectra, which is in good agreement with the theoretical value obtained by *ab initio* calculations. The bond length, dissociation energy, dipole of NaXe and Mulliken charges at Na and Xe in NaXe were calculated, respectively. The spectra of ultraviolet (UV) fluorescence and surface-enhanced Raman scattering of NaXe were also measured.

Keywords: Xenon-ion-implanted NaCl crystal, NaXe, chemical shift, *ab initio* calculation.

In this paper all NaCl crystal samples containing metallic sodium colloids used in experiments were cleaved to ~1mm thickness from a block of NaCl single crystal at room temperature^{1,2}. Two parallel large surfaces of each crystal were polished. Then these NaCl crystal specimens were implanted at 10⁻⁶ Torr with xenon ions using an accelerating voltage of 36 keV. The xenon ion fluences were in the range from 1×10¹⁵/cm² to 7×10¹⁷/cm². The chemical shifts of ²³Na in these NaCl crystal specimens were measured by NMR spectrometer Bruker MSL-400 with NMR-frequency 105.8 MHz at a magnetic field 9.395T. The chemical shift of ²³Na in NaCl water solution is taken as the external standard and the chemical shift of ²³Na in single crystal is equal to 7.1 ppm. The chemical shifts of ²³Na in NaCl crystal specimens implanted with 36-keV xenon ions at fluences from 1×10¹⁷/cm² to 7×10¹⁷/cm² are -9.6 ~ -10ppm. Therefore, the chemical shift of ²³Na in solid state NaXe relative to ²³Na in NaCl single crystal is approximately equal to -17 ppm.

In *ab initio* calculations we used the program packages GAUSSIAN 94 including 3-21G basis set, unrestricted Hartree-Fock (UHF) method for the structural optimization of NaXe and the *ab initio* gauge invariant atomic orbital (GIAO) approach for the calculation of magnetic shieldings (MS) of ²³Na in NaCl and in NaXe, respectively³. The chemical shift of ²³Na in NaXe relative to ²³Na in NaCl is equal to the difference of both magnetic shieldings. Calculated results were listed in **Table 1**.

The calculated chemical shift of ²³Na in NaXe relative to ²³Na in NaCl is -19.5 ppm. The calculated chemical shift -19.5 ppm is in good agreement with the experimental

value -17 ppm. A negative value of chemical shift means a stronger magnetic shielding in excimer NaXe than in NaCl, which is equivalent to an upfield or low-frequency shift. **Table 1** clearly indicates that there is a small, but significant charge transfer (~ 0.006 electrons) from 5p- of Xe to 3s- atomic orbital of Na to explain the upfield ^{23}Na NMR shift in excimer NaXe relative to ^{23}Na in NaCl. Therefore, the chemical bonding in NaXe can be attributed to the partial overlap of 5p- of Xe with 3s- wave function of Na. Our calculated bond length and dissociation energy of NaXe are equal to 5.9 \AA and 0.010eV , respectively, which is in agreement with the atom-atom pair energy 0.012eV of Na-Xe predicted by Cvetko *et al.* in terms of a new phenomenal atom-atom pair potentials model⁴.

Table 1 Calculated results for the characteristics of NaXe clusters

R(Na-Xe) (\AA)	E(UHF) (a.u.)	MS of ^{23}Na (ppm)	Dipole (Debye)	Na charge (e)	Xe charge (e)
1.00	-7356.842366	603.8966	3.745	-0.368161	0.368161
2.00	-7361.418707	515.9009	4.1337	-0.054464	0.054464
3.15	-7361.597760	612.7202	3.1699	-0.058697	0.058697
3.50	-7361.602377	623.5182	2.473	-0.042444	0.042444
4.00	-7361.605092	625.8510	1.5577	-0.023471	0.023471
4.50	-7361.606232	624.1566	0.9049	-0.013396	0.013396
5.06	-7361.606860	623.6596	0.4738	-0.008831	0.008831
5.8.	-7361.607134	624.3292	0.2048	-0.006211	0.006211
5.90	-7361.607138	624.3946	0.1834	-0.005892	0.005892
6.00	-7361.607136	624.4467	0.1643	-0.005567	0.005567
6.50	-7361.607072	624.5400	0.0946	-0.003920	0.003920
7.00	-7361.606975	624.4820	0.0529	-0.002434	0.002434
8.00	-7361.606832	624.3514	0.0135	-0.000646	0.000646
10.00	-7361.606771	624.3084	0.0003	-0.000013	0.000013
Infinity	-7361.606770	624.3079	0.0000	0.000000	0.000000

The spectra of UV fluorescence and surface-enhanced Raman scattering of NaXe were also measured. The 355nm-UV-stimulated emission makes the solid state NaXe clusters possible to be prepared as UV-micro-excimer-laser.

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References

1. J. R. W. Weerkamp, J. C. Groote, J. Seinen, H. W. dem Hartog, *Phys. Rev.* **1994**, *B 50*, 9781.
2. J. Liang, X. Le, Z. Liu, X. Sun, X. Zeng, H. Gu, Y. Li, *Chin. Phys. Lett.* **1999**, *16*, 563.
3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al.* *Gaussian 94, Revision E. 1*, Gaussian, Inc., Pittsburgh PA, **1995**.
4. D. Cvetko, A. Lausi, A. Morgante, *et al.* *J. Chem. Phys.* **1994**, *100*, 2052.

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