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An *ab initio* potential energy surface and vibrational energy levels of HXeI

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ABSTRACT

A three-dimensional potential energy surface of the electronic ground state HXeI is constructed from more than 4200 *ab initio* points at the internally contracted multi-reference configuration interaction with the Davidson correction (icMRCI + Q) level employing large basis sets. The calculations indicate that the linear HXeI molecule is metastable with a barrier of 0.365 eV in the atomization (HXeI → H + Xe + I) channel and a barrier of 1.306 eV in the dissociation (HXeI → HI + Xe) channel. Low-lying vibrational energy levels of both HXeI and DXeI are calculated on the three-dimensional potential energy surface using the Lanczos algorithm, and found to be in good agreement with known experimental band origins.

1. Introduction

During the past decade, a new class of rare-gas-containing charge-transfer molecules have been prepared in a series low-temperature rare-gas matrix experiments [1–9], which has reinvigorated and expanded the field of rare-gas chemistry. These molecules are formed from neutral atomic or molecular fragments with a common formula HRgY, where Rg is rare-gas atom and Y represents a s strongly electronegative species like halogen, OH, CN, or SH. A typical example is HXeI, which has played a major role in revealing the formation and decomposition mechanisms of HRgY molecules [10–12]. Extensive electronic structure calculations indicated that the HRgY type molecules are stabilized by strong Coulomb attraction within the HRg^+ and Y^- ion pair [13–22]. The ionic character of the HRgY molecules suggests the existence of strong vibrational transitions that provide effective detection by infrared absorption spectroscopy [23–25]. The HRgY molecules are metastable compared with the global energy minimum Rg + HY, but it has been experimentally demonstrated that these species decompose producing neutral atoms H + Rg + Y in solid rare gases [11].

From a computational point of view, the HRgY molecules present a challenging task. The ion-pair nature of these compounds, interaction of different neutral and ionic configurations, relatively weak bonds and relativistic effects are very demanding of computational methods. It has already been shown that the equilibrium structure of HRgY can be achieved at a moderate computational level, but accurate energetics or vibrational properties require higher level multi-reference treatments [15,26,27]. Besides large correlation effects, anharmonic vibrational calculations of HRgY molecules are important both because of their usefulness for experimental identification of these molecules, and because of their relevance to dynamical processes in these systems.

HXeI is one of the first observed HRgY molecules in low-temperature matrices [10–12]. In solid Xe matrix, the fundamental and two overtone bands of H–Xe stretching mode (ν_{H-Xe}, $2\nu_{H-Xe}$ and $3\nu_{H-Xe}$) are at 1193, 2190 and 2950 cm^{-1}, respectively, and suggest that the H–Xe stretching mode appears anharmonic. In order to better understand the infrared spectra of HXeI, anharmonic vibrational spectra of HXeI were calculated using correlation-corrected vibrational self-consistent-field (CC-VSCF) method on a potential energy surface constructed at second-order perturbation theory (MP2) level [28]. However, the ion-pair nature of HXeI compound requires high level multi-reference treatments for an accurate representation of the electronic structure, and MP2 theory is not adequate for describing the electronic dynamic correction of HXeI. Therefore, the multi-reference configuration interaction method is required to investigate the vibrational energy levels of HXeI. Moreover, because the HXeI compound is metastable with respect to dissociation to HI + Xe, it is important to investigate the potential barrier heights in order to determine its predissociation dynamics, the transition state for HXeI → H + Xe + I is also more challenging and requires the use of multi-configurational as well as dynamic correlation treatments.

In this work, we report a potential energy surface of HXeI calculated at the multi-reference configuration interaction (icMRCI) level employing an augmented large basis sets. The low-lying vibrational energy levels were then obtained using a Lanczos algorithm.

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2. Computational details

The three-dimensional adiabatic potential energy surface of the electronic ground state of HXeI has been calculated using the Molpro package [29]. Since the single-configurational method is not adequate for the electronic dynamic correction treatments, the internally contracted multi-reference configuration interaction method with the Davidson correction (icMRCI + Q) was used to calculate the potential energy surface of HXeI [30]. For the H atom, the augmented correlation consistent basis sets (aug-cc-pVTZ) [31–32] was employed. For the Xe atom, averaged relativistic core potentials (AREP) including a spin-orbit potential and 18-valence-electron (18-VE) LaJhon basis set [33] was used. For the I atom, Stuttgart-Dresden-Bonn (SDB) pseudopotentials (ECP46MWB) [34] and 7-valence-electron basis set for ECP46MWB [35] were employed. A total of 121 cGTOs (contracted Gaussian-type orbitals) were generated. All icMRCI + Q calculations were based on state-averaged complete active space self-consistent field (CASSCF) reference wave functions. State-averaged CASSCF calculations include equally weighted 2 $^1A'$ and 1 $^1A''$ states. 16 active electrons and 9 active orbitals were used, including one for H (1s), four for Xe (5s and 5p) and four for I (5s and 5p), denoted as MCSCF (16,9). The inner orbitals were also fully optimized, while constrained to be doubly occupied. The total number of contracted configurations in the MRCI calculations was about 0.62 million, which corresponding to about 15.9 million uncontracted configurations. All calculations were performed in the C_s symmetry framework.

A non-uniform direct product grid in the internal coordinates was selected for the calculation of the potential energy surface. The PES for the HXeI molecule was calculated by varying the bond length R_{HXe} from 2.0 to 10.0 a_0, the bond length R_{XeI} from 3.5 to 12.0 a_0 and the bond angle $\gamma_{\mathrm{H-Xe-I}}$ from 10.0 to 180.0°, which gives a total of about 4200 geometry points. Because a large configuration space is covered in our calculation, the icMRCI + Q may experience convergence difficulties. Under such circumstances, the converged natural orbitals of the nearby geometry were used as the initial guess of the orbitals so that the convergence might be improved. Finally, a three-dimensional spline interpolation provides the potential between the grid points.

The triatomic Hamiltonian with zero total angular momentum can be written in Radau coordinates (R_1, R_2, θ) [36] as:

$$\hat{H} = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial R_1^2} - \frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial R_2^2} - \frac{\hbar^2}{2}\left(\frac{1}{m_1 R_1^2} + \frac{1}{m_2 R_2^2}\right)\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta}\right) + V(R_1, R_2, \theta)$$

where m_1 and m_2 are the atomic masses of H and I, respectively. R_1 and R_2 are the Radau radii corresponding to the internuclear distances of H–Xe and Xe–I, respectively. θ is the enclosed angle between R_1 and R_2 with $\theta = 180°$ corresponding to the linear HXeI. The transformation between Radau coordinates (R_1, R_2, θ) and the internal bond length-bond angle coordinate $(R_{\mathrm{HXe}}, R_{\mathrm{XeI}}, \gamma)$ is well documented [36]. A direct product discrete variable representation (DVR) [37] grid was used in the vibrational energy level calculation. Both R_1 range [3.0,6.5] a_0 and the R_2 range [2.5,4.7] a_0 are covered by 80 sine-DVR grid points, respectively. 100 Gauss-Legendre grid points in the interval [110°, 180°] were used for the angular variable. In addition, the potential cutoff is set to be 3.0 eV. The Lanczos propagation algorithm [38] was employed to calculate the vibrational energy levels by recursively diagonalizing the sparse DVR Hamiltonian matrix. 20,000 Lanczos iterations were carried out to ensure the convergence. Spurious eigenvalues were removed using the method detailed in Ref. [39]. When eigenfunctions were needed, the Lanczos recursion was repeated again [40].

3. Results and discussions

Fig. 1 displays the contour plots of the ground state potential energy surface of HXeI in internal coordinates $(R_{\mathrm{HXe}}, R_{\mathrm{XeI}}, \gamma_{\mathrm{HXeI}})$. The molecular minimum at the linear geometry is clear visible in the upper panel of the figure. This linear minimum is located at $R_{\mathrm{HXe}} = 3.255\ a_0$ and $R_{\mathrm{XeI}} = 5.728\ a_0$. As shown in Table 1, the equilibrium geometry is in good agreement with previous theoretical values [40]. Table 1 lists structural parameters and vibrational properties of HXeI, along with the experimental values and previous results, while a schematic relative energy profile of the decomposition pathways for HXeI is given in Fig. 2.

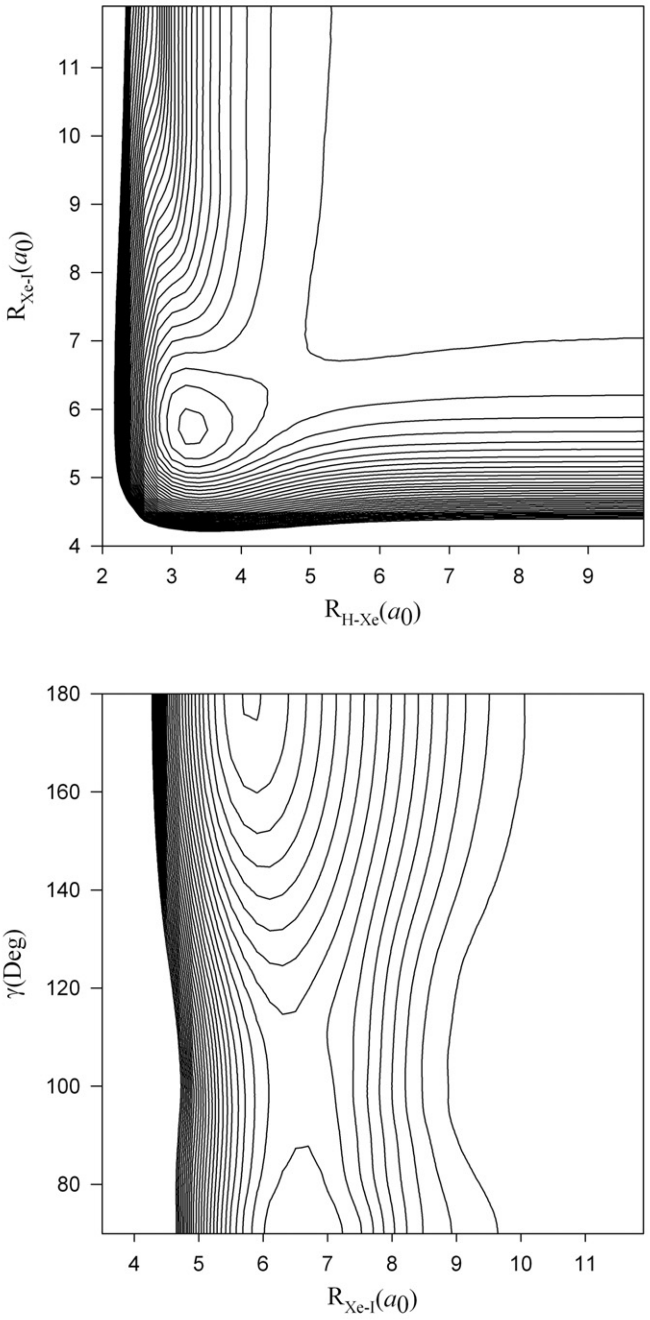

Fig. 1. Contour plots of the potential energy surface of HXeI in internal coordinates. Upper panel, contour plots at $\gamma_{\mathrm{H-Xe-I}} = 180°$. Lower panel, contour plots at $R_{\mathrm{HXe}} = 2.91\ a_0$. Contours are spaced by 0.15 eV. The zero of the energy is defined as the HXeI minimum.