Project Title:

Elucidation of internal energy flow of molecular ions by RIKEN Cryogenic Electrostatic ion storage ring

Name:
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1. Background and purpose of the project, relationship of the project with other projects

Internal energy dynamics plays a crucial role in determining the behavior of molecules, such as dissociation and structural change, particularly in environments like interstellar space. Our project focuses on studying the N_2O^+ triatomic molecular ion and how its internal energy flow is controlled through Fermi resonance, which involves the interaction of different vibrational modes. By comparing our findings with experimental results from the RIKEN Cryogenic Electrostatic Ion Storage Ring, we aim to understand how the vibrational coupling impacts the process of vibrational cooling in small molecules.

2. Specific usage status of the system and calculation method

We performed quantum chemistry calculations in the HBW2 system at an advanced level using the vibrational configuration interaction method. We applied the ab initio calculations of Molpro, a quantum chemical calculation package that utilizes multiple configuration theory. The interplay among configurations with 15 electrons spread over 12 orbitals was described by the Hamiltonian. To accurately determine the potential energy surface of the electronic ground state and the wavefunction of the vibrationally excited state, we compared the results of the Multi Reference Configuration Interaction (MRCI) and Complete Active Space Self-Consistent Field (CASSCF) methods. The MRCI method accurately calculates the excited states considering the electron correlations, but requires a high computational cost. In contrast, the CASSCF method is less computationally expensive.

3. Result

We derived a vibrational spectra based on the electronic ground state calculated from the CASSCF obtained potential energy surfaces. The non-negligible overtone contributions of the stretching oscillations v_1 and v_3 are in sharp contrast to our previous work [Hirota et al., Phys. Rev. **A** 102, 023119 (2020)], which considered only transitions under the selection rules $\Delta v = 1$, $\Delta l = 1$. Accurate calculations of the cooling process must consider not only the Fermi resonances, but also the overtones, combination tones, and intermodal transitions. Our obtained vibrational energies deviated by up to 100 cm^{-1} from the measured value, suggesting that this method is insufficient. To improve this scenario, we applied the MRCI method, which accurately incorporates the electron correlations. Comparing the potentials of the MRCI and CASSCF calculations, one observes that the electron correlation significantly affects the potential energy of the O–NN stretching vibration mode (v_1). After obtaining the potential energy surface, we applied the vibrational configuration interaction (VCI) program SINDO [Yagi, Mol. Sci. **10**, A0085 (2016)], which is suitable forvibration analysis involving anharmonicity.

4. Conclusion

The calculated vibrational energies were much closer to the experimental results than those of the CASSCF method, suggesting that the MRCI calculation is more suitable for N_2O^+, where the electron correlation is important. However, as the Renner–Teller effect is not included a priori in the present calculation, the calculated vibrational energy of the (1 2 0) state deviates by approximately 50 cm^{-1} from the experimental values. Consequently, our calculations did not properly reproduce the Fermi resonance, which is sensitive to vibrational energy. As the transition intensity is proportional to n/ϵ^3 under the harmonic approximation (where n is the number of quanta and ϵ is the energy spacing between the states), a discrepancy of approximately 0.5 s^{-1} is expected in the A coefficients.

5. Schedule and prospect for the future

It was not possible to reproduce experimental results for both X 3/2 and X 1/2 states simultaneously. The reason may be that the spin-orbit and rovibronic interactions were treated using approximations. Performing calculations that fully account for these interactions without the approximations would require significant computational resources. Therefore, a theoretical treatment fully incorporating these contributions and the vibronic and spin-orbit interactions remains challenging.

Usage Report for Fiscal Year 2024

Fiscal Year 2024 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

"Fermi resonance in the radiative vibrational cooling dynamics of N_2O^+"

S. Harayama*, S. Kuma, N. Kimura, K. C. Chartkunchand, M. Baba, T. Murakami, T. Takayanagi, K. Yagi, Y. Nakano, T. Yamaguchi, and T. Azuma*

Phys. Rev. A **111**, 032803 (2025). DOI: 10.1021/acs.jpca.4c08362

[Conference Proceedings]

[Oral presentation]

"極低温静電型イオン蓄積リング RICE を用いた N_2O^+の輻射振動冷却 VIII"

原山朔弥, 木村直樹, 久間晋, Kiattichart Chartkunchand, 馬場正昭, 村上龍大, 高柳敏幸, 山口貴之, 中野祐司, 東俊行

日本物理学会第 79 回年次大会, 北海道大学（札幌）、2024 年 9 月 16－19 日.

[Poster presentation]

"極低温イオン蓄積リングを用いた直線 3 原子分子イオン N_2O^+のフェルミ共鳴準位を介する輻射振動冷却過程の測定"

原山朔弥、木村直樹、久間晋、Kiattichart Chartkunchand、馬場正昭、村上龍大、高柳敏幸、山口貴之、中野祐司、東 俊行

第 20 回 AMO 討論会, 理研（和光）、2024 年 6 月 7&8 日.

"極低温イオン蓄積リングを用いた直線 3 原子分子イオン N_2O^+のフェルミ共鳴準位を介する輻射振動冷却過程の測定 III"

原山 朔弥, 木村 直樹, 久間 晋, Kiattichart Chartkunchand, 馬場 正昭, 村上龍大, 高柳敏幸, 山口 貴之, 中野 祐司, 東 俊行

原子衝突学会第 49 回年会, 奈良女子大学（奈良）、2024 年 8 月 7－9 日.

[Others (Book, Press release, etc.)]