

New features in the ionic states of N_2O_4 : Experimental and theoretical study

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Synopsis We present a combined experimental and theoretical study focused on the ionic states of the N_2O_4 molecule. Experimental results regarding photoionization induced by the synchrotron radiation SOLEIL in the 13.5-15.5 eV energy range were obtained using the electron-ion velocity vector correlation method. The potential energy curves for the dissociation of the N-N bond were computed within ab initio multireference wave functions based methods (CASSCF and CASPT2) for the first electronic states of N_2O_4 and $N_2O_4^+$.

The dimer of the NO_2 molecule (N_2O_4) has been considered in recent strong-field ionization studies as an example of polyatomic system involving coupled electronic and nuclear dynamics, on an ultrashort time domain [1]. In addition, the N_2O_4 molecule presents a strong electronic correlation [2]. The identification of ionic states is thus a challenge both from the experimental and the theoretical point of view.

We here report on recent experimental results regarding photoionization (PI) of the N_2O_4 molecule in the 13.5-15.5 eV photon excitation energy range, obtained using the vector correlation method [3], which provides for each electron-ion coincident event the emission velocity vectors of the two particles. The experiments were performed on the DESIRS beamline at SOLEIL, using the SAPHIRS supersonic expansion.

In order to gain deeper insight in these experiments potential energy curves for the dissociation of the N-N bond for the neutral N_2O_4 and its cation $N_2O_4^+$, have been calculated at the MS-CASPT2/CASSCF/ANO-L level of theory. The active space of the CASSCF wave function consists of 22/21 electrons in 16 molecular orbitals for the $N_2O_4/N_2O_4^+$ species, respectively.

The experimental results demonstrate that dissociative ionization producing (NO_2^+, e^-) coincident pairs strongly dominates non-dissociative ionization ($N_2O_4^+, e^-$). The branching ratio determined for each ionization channel is of the order of $DPI/NDPI \geq 20$, in average. The electron-ion kinetic energy correlation diagram (KECD) enables us to correlate each $N_2O_4^+$ ionic state identified by the photoelectron energy to a given dissociation channel. The elongated structures observed in the KECD reveal a strong excitation of the internal degrees of freedom of the molecular fragments ($NO_2^+ + NO_2$)

(Figure 1). The photoelectron spectrum, i.e. the projection of the KECD onto the vertical axis, is in good agreement with previous measurements [4]. The $(\mathbf{V}_{NO_2^+}, \mathbf{V}_{e^-})$ vector correlation also provides the asymmetry parameters characterizing electron and ion-fragment emission, as well as the recoil frame photoelectron angular distribution (RFPAD) for each ionization channel. The RFPADs will be presented at the poster: they display significant emission anisotropies, which are signatures of each ionized molecular orbital of the N_2O_4 initial state and of the electronic correlation induced by the ionization process.

From the theoretical calculations (MS-CASPT2 curves), relevant information such as vertical ionization energies to the ground and first excited states of $N_2O_4^+$ and possible dissociation channels has been extracted. An analysis of the energy and character of the electronic states of the fragments (NO_2 and NO_2^+) is crucial to interpret the experiments.

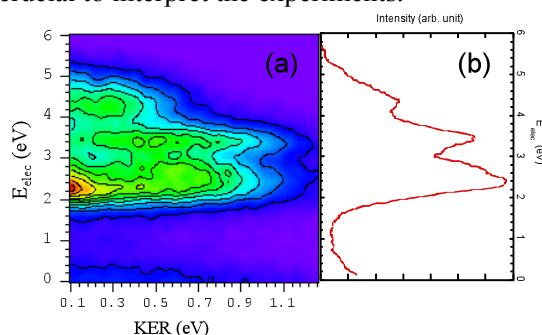


Figure 1. (a) (NO_2^+, e^-) electron-ion KECD for PI of N_2O_4 (b) Photoelectron spectrum, $h\nu \approx 15.7$ eV.

References

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